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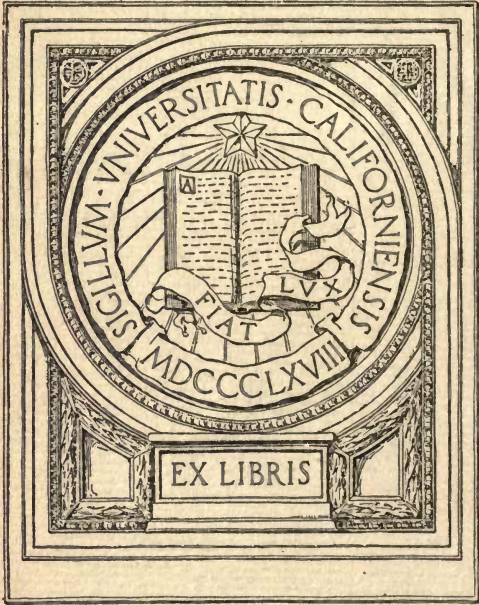


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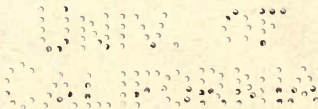
A SIMPLE TREATMENT OF THE SUBJECT
OF CHEMICAL CALCULATIONS

BY

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PREFACE

THE form that this book has taken is due to a very considerable experience of the difficulties encountered by students when attempting to make chemical calculations. The effort has been made to smooth away these difficulties, and to give an accurate, as well as a simple and systematic, treatment of the subject. A number of points are, I venture to think, more clearly presented than in other books; for instance, Charles's Law and the so-called gramme-molecular volume of gases.

The object of the book is to give clear ideas on the subject, but a book that serves this purpose must necessarily give the best help to the student working for examinations that include chemical calculations. Hence many examples are given of questions set in examination papers of a number of important universities in Britain and America. These questions have the advantage of

presenting problems in different ways, so that the student is trained in interpreting different forms of expression. It is hoped that the book may be of service to teachers who find difficulty in making the subject clear, probably because they expect the pupil to understand *intuitively* things which they will find he does not understand unless stated in the simplest form.

The attempt has been made to make the text a continuous line of argument, and therefore some matters that are frequently inserted as an integral part of a book on calculations have been thrown into an appendix.

A collection of equations in common use appeared advisable, and the plan of designating *gases* in some way is, I think, a good one.

I wish to thank Professor H. L. Wells of the Sheffield Scientific School of Yale University for the kindly interest that he has taken in this little volume and for his valuable suggestions, particularly in regard to the chapter on volumetric analysis.

J. W.

NEW YORK,

February, 1899.

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THE ARITHMETIC OF CHEMISTRY

CHAPTER I

CALCULATION WEIGHTS OF ELEMENTS

WHEN potassium chlorate is heated strongly enough, oxygen is given off and potassium chloride is left behind. The weight of the oxygen given off is 39.18% of the original chlorate, and the potassium chloride is 60.82%. For every 100 ounces or pounds or grammes¹ of chlorate taken, 39.18 ounces or pounds or grammes of oxygen are evolved, and 60.82 ounces or pounds or grammes of potassium chloride remain behind.

These numbers give the ratio that exists between the quantities of the different substances in every case, and so if we wish to know how much oxygen can be obtained from 18 ounces or pounds or grammes of potassium chlorate, we require merely

¹ For the system of French measures see Appendix A.

to multiply 18 by $\frac{39.18}{100}$ and obtain as answer 7.053 ounces or pounds or grammes. The potassium chloride left behind is, naturally,

$$18 - 7.053 = 10.947 \text{ ounces or pounds or grammes.}$$

In the same way, when pure marble, which is calcium carbonate, is heated, carbon dioxide is given off, and lime is left behind; 44% of the marble is carbon dioxide and 56% is lime. If we wish to know how much lime will be left if 65 ounces or pounds or grammes are heated, we require merely to multiply 65 by $\frac{56}{100}$ and obtain as answer 36.4 ounces or pounds or grammes.

Conversely, if the problem be to determine how much potassium chlorate is required to produce 48 ounces or pounds or grammes of oxygen, it is evident that we must multiply 48 by $\frac{100}{39.18}$, because we require 100 ounces or pounds or grammes of chlorate for every 39.18 ounces or pounds or grammes of oxygen.

$$48 \times \frac{100}{39.18} = 122.5 \text{ ounces or pounds or grammes.}$$

Likewise, if the problem be to determine how

much marble is required to produce 35 ounces or pounds or grammes of carbon dioxide, it is evident that $35 \times \frac{100}{44} = 79.54$ ounces or pounds or grammes is the answer.

Water consists of 11.11% hydrogen and 88.89% oxygen, and 36 ounces or pounds or grammes of water contain

$$36 \times \frac{11.11}{100} = 4 \text{ ounces or pounds or grammes of hydrogen,}$$

and

$$36 \times \frac{88.89}{100} = 32 \text{ ounces or pounds or grammes of oxygen.}$$

Carbon dioxide is composed of 27.27% carbon and 72.73% oxygen, therefore to produce 60 ounces or pounds or grammes of carbon dioxide,

$$60 \times \frac{72.73}{100} = 43.64 \text{ ounces or pounds or grammes of oxygen are required.}$$

Now analysis and synthesis of substances give us merely such data as have been presented above, but chemical problems are rarely worked out in this form. The reason is this :

In order to work a problem in any case, it would be necessary to know the percentage composition of

the substance in question, and if one were called upon to remember the percentage composition of even the ordinary substances, the memory would be severely taxed. It is found that by assigning a definite value to each element, calculations involve less tax upon the memory, and moreover provide for a reasonable theory as to the structure of matter. For the purpose of calculations, however, the theoretical development may be left out of sight.

In the percentage composition of water given above, it will be seen that the weight of oxygen is 8 times as much as that of the hydrogen, or $\frac{8}{9}$ of the total weight of water; and the problem to determine how many ounces or pounds or grammes of oxygen are in 36 ounces or pounds or grammes of water, is solved by multiplying 36 by $\frac{8}{9}$.

$$36 \times \frac{8}{9} = 32 \text{ ounces or pounds or grammes of oxygen.}$$

Carbon dioxide, as we saw, contains 72.73% of oxygen; carbon monoxide contains 57.14%. Since the monoxide contains less oxygen than the dioxide, let us take the number 8 (which we used in the case of water) to represent the weight of oxygen in

carbon monoxide, and let us now calculate how much carbon is united to 8 ounces or pounds or grammes of oxygen in carbon monoxide.

Carbon monoxide contains 57.14% of oxygen and 42.86% of carbon, therefore the carbon weighs $\frac{42.86}{57.14}$ as much as the oxygen; and as the weight of the oxygen was 8, the weight of the carbon must be

$$8 \times \frac{42.86}{57.14} = 6;$$

therefore 6 ounces or pounds or grammes of carbon are united with 8 ounces or pounds or grammes of oxygen in carbon monoxide. Carbon monoxide burns in oxygen, to form carbon dioxide, and so if we start with 6 ounces or pounds or grammes of carbon, it can be first converted into carbon monoxide, and then still farther into dioxide. But the carbon in carbon dioxide is 27.27%, the oxygen being 72.73%. The problem now is to determine how much oxygen is united with 6 ounces or pounds or grammes of carbon in carbon dioxide. For this we have

$$6 \times \frac{72.73}{27.27} = 16 \text{ ounces or pounds or grammes of oxygen.}$$

For 6 parts by weight of carbon, there is in carbon monoxide 8 parts by weight of oxygen, and in carbon dioxide 16 parts by weight of oxygen, or twice as much in the second case as in the first. In fact, this is the meaning of the names given to the two gases, and, till this relationship was discovered, the names could not have been given. (The gases were called originally by other names which did not show their relationship.)

Carbon is combined with hydrogen in marsh gas; 75% being carbon and 25% hydrogen. For every 6 ounces or pounds or grammes of carbon, there are, therefore, 2 ounces or pounds or grammes of hydrogen. In acetylene (the gas which has lately come into prominence as an illuminant) 92.3% of carbon is united with 7.7% of hydrogen, that is, 6 ounces or pounds or grammes of carbon is united with $\frac{1}{2}$ ounce or pound or gramme of hydrogen, or *twelve* parts by weight of carbon, with *one* part by weight of hydrogen. In all of these calculations, we have found that the numbers to be used for hydrogen, oxygen, and carbon, respectively, are 1, 8, and 6, or multiples of these numbers. If the ordinary symbols be used to represent the elements,

then 9 ounces or pounds or grammes of water might be represented by the formula HO; 14 ounces or pounds or grammes of carbon monoxide by the formula CO; and 22 ounces or pounds or grammes of carbon dioxide by the formula CO₂. But it is found that while by *electrolysis* of water all of the hydrogen that is in the water is set free as a gas, and $\frac{1}{9}$ of the weight of water decomposed is hydrogen; on the other hand, when sodium acts on water, only one-half as much hydrogen is set free, that is, $\frac{1}{18}$ of the weight of the water acted upon. For this and a number of other reasons, it is considered better to take as our standard weight of water, 18 ounces or pounds or grammes, of which 2 are hydrogen and 16 are oxygen, and this quantity is represented by the formula H₂O, and 16 ounces or pounds or grammes represent the standard weight of oxygen. In the same way, the standard weight of carbon is 12, and the formula CO represents 28 ounces or pounds or grammes of carbon monoxide, and CO₂ represents 44 ounces or pounds or grammes of carbon dioxide.

Just as there is a standard number for hydrogen, oxygen, and carbon, so there is for potassium,

chlorine, iron, zinc, and all the elements. These numbers are usually called atomic weights and are considered as connected with the atomic theory, but if the whole atomic theory were proved unfounded, these standard numbers could still be used for calculations, and we may call them calculation weights. One-half of the difficulty experienced by the beginner in making calculations is that he uses his symbols and formulæ in a loose, slipshod, and unscientific manner.

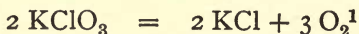
It is inaccurate to say H_2O is a colourless, tasteless liquid; CO_2 is a poisonous gas; NH_3 has a pungent odour. H_2O represents 18 parts by weight, be it ounces or pounds or tons or grammes or kilogrammes of water. CO_2 represents 44 parts by weight of carbon dioxide, and NH_3 represents 17 parts by weight of ammonia, and the symbols should never be used instead of the name of the substance (by any one, at all events, that has the slightest difficulty in chemical calculations).

CHAPTER II

SIMPLE CALCULATIONS OF WEIGHTS

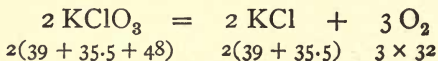
IN making chemical calculations, it is necessary to know the formulæ employed for the standard weights of the substances which enter into the reaction. It is also necessary to know the calculation weights of each of the elements composing the substances, in order to determine the standard weights of the substances themselves. It is, thirdly, necessary to know the nature of the chemical reaction which takes place and to be able to express it quantitatively as is done by a chemical equation. For instance, if we are to calculate how much oxygen can be obtained from a given quantity of potassium chlorate, we must know the formula of the standard weight of potassium chlorate; namely, KClO_3 . For our purpose now, it is unimportant to know *why* the formula KClO_3 is given and not $\text{K}_2\text{Cl}_2\text{O}_6$, which would have exactly the same percentage composition. We must, *secondly*, know the calculation weights of K, Cl, and O. We

thirdly require the equation which represents the action that takes place when potassium chlorate is heated; namely,



The calculation weight of K is 39, of Cl is 35.5, and of O is 16.

The equation then represents



or, expressed in words,

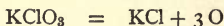
$2 \times 122.5 = 245$ ounces or pounds or grammes of potassium chlorate yield

$2 \times 74.5 = 149$ ounces or pounds or grammes of potassium chloride,

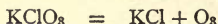
and

$3 \times 32 = 96$ ounces or pounds or grammes of oxygen.

¹ We are not yet in a position to discuss why this equation is better than



or



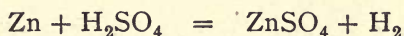
Either of these would be sufficient for the calculation we have at present in hand, but in order to avoid having to revise the form of the equation later on, it is given as above.

If now we are asked to calculate how much oxygen can be obtained from 18 ounces or pounds or grammes of potassium chlorate, we have

$$18 \times \frac{96}{245} = 7.053 \text{ ounces or pounds or grammes of oxygen,}$$

the same result as was obtained before (page 2).

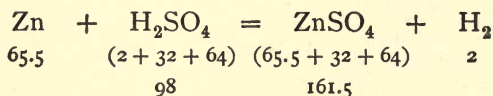
When hydrogen is obtained by the action of zinc on sulphuric acid, we have the equation



It should never be forgotten by the student that equations are not arrived at in a purely algebraic fashion. They merely represent, in symbols, quantitative relationships that have been discovered by experiment. For example, the above relationship holds only if the sulphuric acid be dilute. If it be strong, other substances besides hydrogen are formed, such as hydrogen sulphide, sulphur dioxide, and sulphur. An equation rarely represents the entire chemical reaction, but it represents the chief one under certain conditions, and in carrying out the experiment the endeavour is made to secure the proper conditions. The water that is used to dilute

the sulphuric acid is not mentioned in the equation, because its amount is unchanged by the reaction. The equation, coupled with the calculation weights of the different elements, provides the data necessary for the solving of problems.

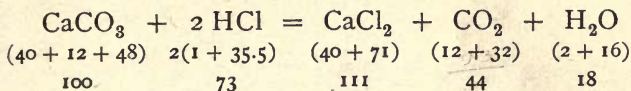
The equation is, in this case,



That is, 65.5 grammes¹ of zinc acting on 98 grammes of sulphuric acid produces 161.5 grammes of zinc sulphate and 2 grammes of hydrogen. From the information provided by the equation, it is possible to make any calculations which involve merely the *weights* of these four substances; for instance, how much zinc is required in the preparation of 10 grammes of hydrogen, or how much zinc sulphate would be obtained by the action of 150 grammes of sulphuric acid on zinc, and how much zinc would be left unacted on, if 200 grammes of zinc had been used in the last case?

¹ The English weights, such as ounces and pounds, are unusual in scientific chemistry, and are therefore omitted in the sequel.

In the preparation of carbon dioxide, marble is acted on by hydrochloric acid, and the equation is



If the question is asked, how much hydrochloric acid is required for the preparation of 60 grammes of carbon dioxide, we have

$$60 \times \frac{73}{44} = 99.54 \text{ grammes,}$$

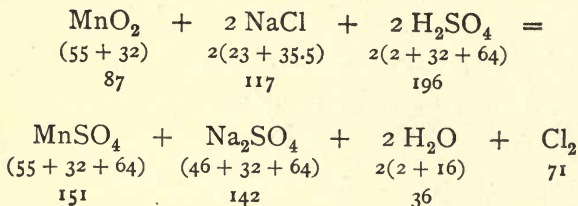
since the equation shows us that 73 grammes of hydrochloric acid are required to produce 44 grammes of carbon dioxide.

If it be required to calculate how much calcium chloride is obtained from 85 grammes of calcium carbonate, we have

$$85 \times \frac{111}{100} = 94.34 \text{ grammes,}$$

since the equation shows that 111 grammes of calcium chloride are obtained from 100 grammes of calcium carbonate. It is easy to calculate also how much hydrochloric acid would be required for this operation, and how much carbon dioxide would be obtained.

In the equation



we have data for a multitude of chemical problems.

EXAMPLES

1. Calculate the percentage composition of potassium nitrate (KNO_3). (Mason Science Coll., 1883, and Columbia Univ., 1895.) This is equivalent to asking how much of each element 100 grammes of potassium nitrate contains, and from the formula it is known that 101 grammes contain 39 grammes of potassium, 14 grammes of nitrogen, and 48 grammes of oxygen.

Ans. 38.61% potassium; 13.86% nitrogen; 47.53% oxygen.

2. Calculate the percentage composition of calcium sulphate (CaSO_4). (Columbia Univ., 1898.)

Ans. 29.4% calcium; 23.5% sulphur; 47.1% oxygen

3. Calculate the percentage of oxygen in: (a) water, (b) manganese dioxide, and (c) potassium chlorate. (Princeton Univ. School of Science, 1893.)

Ans. (a) 88.89; (b) 36.87; (c) 39.18.

4. What weight of oxygen can be obtained from 408 grammes of potassium chlorate? (Mason Coll.)

Ans. 160 grammes.

5. How many pounds of nitric acid can be obtained by the distillation of 180 lbs. of nitre with sufficient sulphuric acid? (Mason Coll.)

Ans. 112.3 lbs.

6. Oxide of mercury is heated: (1) alone, (2) with carbon, (3) with hydrogen. What products are formed, and what weight of each would be obtained, if 10 grammes of mercuric oxide were used? (Lond. Matric.)

(1) oxygen, 0.741 gramme; (2) carbon dioxide, 1.019; (3) water, 0.834.

7. How much hydrogen and oxygen is contained in 180 kilogrammes of water? (Princeton Univ.)

Ans. 20 kilogrammes hydrogen; 160 kilogrammes oxygen.

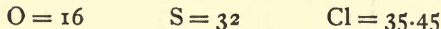
8. Calculate the percentage of carbon, hydrogen, and oxygen in a compound of the formula $C_{12}H_{22}O_{11}$. (Lond. Matric.)

Ans. Carbon, 42.1%; hydrogen, 6.4%; oxygen, 51.5%.

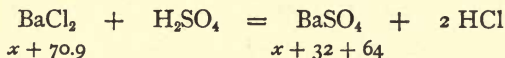
9. 100 grammes of hydrochloric acid are mixed with 100 grammes of dissolved caustic soda. What will be the weight of the compounds contained in the resulting solution? (The Yorkshire Coll.) There is more acid than is required to neutralize the soda, hence there will be both sodium chloride and hydrochloric acid.

Ans. Sodium chloride, 146.25 grammes; hydrochloric acid, 8.75 grammes.

10. If 100 parts of barium chloride give 112.1 of barium sulphate, what is the atomic weight of barium? (The Yorkshire Coll. Scholarship Exam., 1895.)



This problem is really to calculate the value of x in the equation



and we are told that the ratio of the chloride to sulphate is 100 : 112.1.

Therefore $\frac{x + 70.9}{x + 32 + 64} = \frac{100}{112.1}$, whence $x = 136.7$. *Ans.*

11. If 75 c.c. of a solution of hydrochloric acid are neutralized by 60 c.c. of a solution of sodium hydroxide containing 0.003 gramme of the alkali per cubic centimetre, what weight of the acid is contained in 1 c.c. of its solution? (Cornell Univ., December, 1897.)

60 c.c. of alkaline solution contains $60 \times 0.003 = 0.18$ gramme of sodium hydroxide, which requires

$$\frac{36.5}{40} \times 0.18 = 0.1642 \text{ gramme of acid,}$$

which is contained in 75 c.c.; therefore 1 c.c. contains 0.00219 gramme hydrochloric acid.

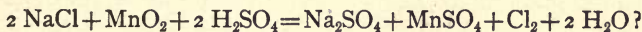
12. A solution of potassium hydroxide contains 0.02 gramme of alkali per cubic centimeter, and 15 c.c. of it exactly neutralize 40 c.c. of a solution of hydrochloric acid.

How many grammes of hydrochloric acid are contained in 15 c.c. of the acid solution? (Cornell Univ., 1898.)

Ans. 0.0733 gramme.

13. A solution of potassium hydroxide contains 0.01 gramme of alkali per cubic centimeter, and 10 c.c. of it exactly neutralize 40 c.c. of a solution of hydrochloric acid. How many grammes of hydrochloric acid are contained in 15 c.c. of the acid solution? *Ans.* 0.0244 gramme.

14. What weight of chlorine can be produced from 100 grammes of common salt by the reaction



(Cornell Univ., September, 1895.) *Ans.* 60.7 grammes.

CHAPTER III

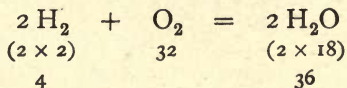
MORE COMPLEX CALCULATIONS OF WEIGHTS

MORE complex problems than those already given may present themselves.

Problem.—How many grammes of potassium chlorate are required to produce enough oxygen for the complete combustion of 10 grammes of hydrogen?

Two chemical reactions are spoken of in this problem, and it is necessary to know the nature of each reaction, and to be able to express it by an equation. The hydrogen is to be burned, and enough oxygen must be supplied for the purpose. This oxygen is to be obtained from potassium chlorate, of which a requisite quantity must be provided. In the first place, then, we have to consider that 10 grammes of hydrogen are to be burned; that is, are to unite with oxygen to form water.

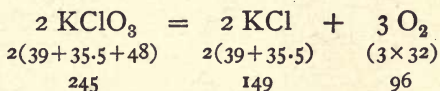
The equation



supplies the data necessary for determining the quantity of oxygen, for we are told by it that 4 grammes of hydrogen require 32 grammes of oxygen; 10 grammes of hydrogen therefore require

$$10 \times \frac{32}{4} = 80 \text{ grammes of oxygen.}$$

The oxygen is obtained from potassium chlorate as represented by the equation



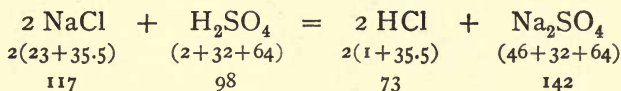
which shows that to produce 96 grammes of oxygen, 245 grammes of potassium chlorate must be taken. But the problem stipulates for the providing of 80 grammes of oxygen, therefore $245 \times \frac{80}{96} = 204.2$ grammes of potassium chlorate¹ are required.

Another problem of the same nature.

Problem. — How much carbon dioxide can be set free from marble by the hydrochloric acid obtained from 30 grammes of common salt? The solving of this problem involves the knowledge of how hydrochloric acid is obtained from common salt; and also of how hydrochloric acid acts on marble. When sul-

¹ See Appendix B.

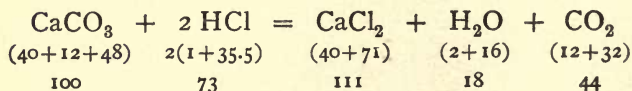
phuric acid is put upon common salt and the mixture strongly enough heated, the reaction takes place in the manner shown by the equation



117 grammes of common salt produce 73 grammes of hydrochloric acid, therefore 30 grammes of common salt (the amount given in the problem) will produce

$$\frac{30}{117} \times 73 = 18.7 \text{ grammes of hydrochloric acid.}$$

The equation

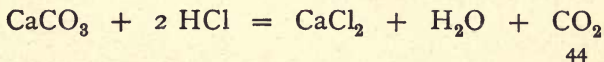


shows that 73 grammes of hydrochloric acid set free 44 grammes of carbon dioxide; therefore, 18.7 grammes of hydrochloric acid would set free

$$\frac{18.7}{73} \times 44 = 11.27 \text{ grammes of carbon dioxide.}$$

These equations, as put down above, give a great many more data than are necessary for the problem

in hand. It is advisable for the beginner to write out equations in full with the numerical values for each term; but when familiarity with the process is gained it is much neater to see what is needed and to make no more calculations than are necessary. In the last problem the only substances whose quantity is referred to are carbon dioxide, hydrochloric acid, and common salt; and though the quantity of hydrochloric acid is referred to, we are not asked to determine that quantity, though we did so in working out the problem. This is not necessary, however, as may be seen by a consideration of the two equations



These two equations as just written show that 117 grammes of common salt produce 73 grammes of hydrochloric acid, and that 73 grammes of hydrochloric acid acting on marble produce 44 grammes of carbon dioxide; so that 117 grammes of sodium chloride produce enough hydrochloric acid to liberate 44 grammes of carbon dioxide. Thirty grammes of

common salt will therefore produce enough hydrochloric acid to liberate

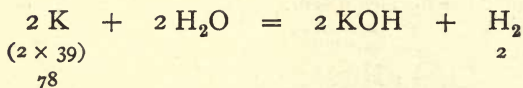
$$44 \times \frac{30}{117} = 11.27 \text{ grammes of carbon dioxide,}$$

which is the same result as already obtained.

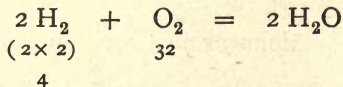
Another example of the same nature.

Problem. — How much potassium must act on water in order to produce enough hydrogen to combine with 6 grammes of oxygen?

Potassium acts on water according to the equation



and hydrogen combines with oxygen according to the equation



The problem may be worked out at full length, but by inspection of the second equation it may be seen that 32 grammes of oxygen require 4 grammes of hydrogen; and by inspection of the first equation, that in order to produce 2 grammes of hydrogen,

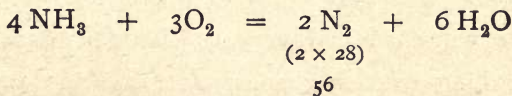
78 grammes of potassium are required, and therefore to produce 4 grammes of hydrogen $78 \times 2 = 156$ grammes of potassium are required.

156 grammes of potassium are therefore required to produce enough hydrogen to combine with 32 grammes of oxygen, and hence, in order to produce enough hydrogen to combine with 6 grammes of oxygen $156 \times \frac{6}{32} = 29.25$ grammes of potassium are required.

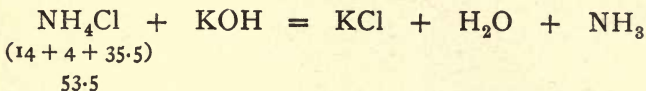
It is evident that the above problem might be enlarged by the inquiry how much hydrogen would be left over if 36 grammes of potassium had been used, and it would merely remain to calculate how much hydrogen is produced by the action on water of $36 - 29.25 = 6.75$ grammes of potassium.

Problem. — How much nitrogen is produced by the complete combustion of the ammonia obtained by the action of caustic potash on 15 grammes of ammonium chloride?

Ammonia burns according to the equation



and is produced from ammonium chloride according to the equation



The first equation shows that 56 grammes of nitrogen are produced by the combustion of four times the formula weight of ammonia. The second equation shows that 53.5 grammes of ammonium chloride are required to yield the formula weight of ammonia, and therefore $53.5 \times 4 = 214$ grammes of ammonium chloride are required to yield *four times* the formula weight of ammonia. Therefore 214 grammes of ammonium chloride give 56 grammes of nitrogen; 15 grammes of ammonium chloride will therefore give

$$56 \times \frac{15}{214} = 3.93 \text{ grammes of nitrogen.}$$

In these equations we have set down the formula weights of two substances only. Of these the problem gives the actual weight used of one, and asks for the actual weight obtained of the other.

One who has had very considerable experience in working problems would see that the problem

above, expressed in its simplest terms, involves merely the question how much nitrogen is contained in 15 grammes of ammonium chloride, because the second equation shows that all of the nitrogen in ammonium chloride is obtained as ammonia; and the first equation shows that all of the nitrogen in ammonia is set free in the combustion. For solving this problem we need merely use the calculation weights in the formula of ammonium chloride, and see that 53.5 grammes of ammonium chloride contain 14 grammes of nitrogen, and therefore 15 grammes of ammonium chloride contain

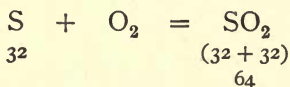
$$14 \times \frac{15}{53.5} = 3.93 \text{ grammes of nitrogen,}$$

the same result as already obtained.

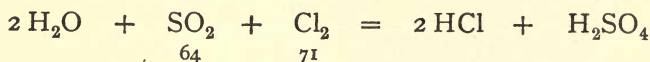
The problem may involve still more chemical reactions and become still more complicated. (Such complicated problems, though seldom set in examinations, are a splendid exercise for the student.)

Problem. — Ten grammes of sulphur are burned in oxygen, and the sulphur dioxide produced entirely dissolved in water. How much manganese dioxide is required to produce enough chlorine to oxidize the sulphur dioxide to sulphuric acid?

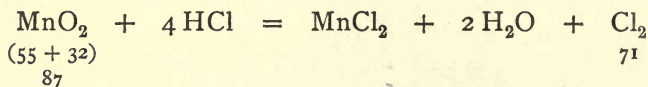
Here three distinct chemical reactions are involved, and we need, therefore, three equations to provide the necessary data. Sulphur burns in oxygen according to the equation



Chlorine acts on sulphur dioxide in water according to the equation



and manganese dioxide produces chlorine according to the equation



The equations show that 32 grammes of sulphur produce 64 grammes of sulphur dioxide, which require for conversion into sulphuric acid, 71 grammes of chlorine, which are produced by the action of hydrochloric acid on 87 grammes of manganese dioxide. Since 32 grammes of sulphur require 87 grammes of manganese dioxide, 10 grammes of sulphur will require

$$87 \times \frac{10}{32} = 27.19 \text{ grammes of manganese dioxide.}$$

EXAMPLES

1. The hydrogen obtained from 6.55 grammes of zinc (acted on by acid) is passed over heated mercuric oxide. What weight of water is produced and how much mercury?

Ans. 1.8 grammes water ; 20 grammes mercury.

2. What weight of potassium nitrate is required to produce enough nitric acid to make 10 grammes of cupric nitrate from cupric oxide ?

Ans. 10.77 grammes.

3. How much calcium carbonate could be made from the carbon dioxide obtained by heating 15 grammes of oxalic acid (anhydrous) with strong sulphuric acid?

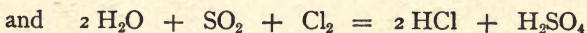
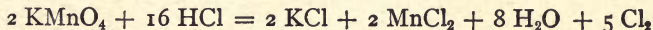
Ans. 16.67 grammes.

4. What amount of ammonium nitrate would produce enough nitrous oxide for the complete combustion of 36 grammes of carbon?

Ans. 480 grammes.

5. If 10 grammes of potassium permanganate were distilled with a concentrated solution of hydrogen chloride, and the evolved gas were passed into a solution of sulphur dioxide, what amount of sulphuric acid would be produced? (Lond. Univ. Inter. Sci., 1893.)

The equations are



These equations show that $2 \times 158 = 316$ grammes of permanganate provide enough chlorine to produce $5 \times 98 = 490$ grammes of sulphuric acid, therefore 15.5 grammes sulphuric acid is the amount produced by the 10 grammes of permanganate.

CHAPTER IV

THE VOLUME OF GASES

WHILE it is possible to make calculations for the *weights* of solids, liquids, and gases involved in a chemical reaction, it is also possible to make calculations for the *volumes* of *gases*, though not for the volumes of liquids and solids.

As, however, the volume of a gas changes with its pressure and temperature, it is necessary to state always at what pressure and temperature the gases are measured. Before attempting to make calculations, it will be necessary to consider the manner in which pressure and temperature affect the volume.

EFFECT OF PRESSURE

Sir Robert Boyle, in the year 1662, showed that when the temperature of a gas remains constant, the volume varies inversely as the pressure. If a quantity of air, for example, has a volume of 10 gallons or 10 cubic feet or 10 litres, at the ordinary atmospheric pressure, it would have a volume of 5

gallons or 5 cubic feet or 5 litres, at 2 atmospheres' pressure, and 20 gallons or 20 cubic feet or 20 litres, at one-half of an atmosphere's pressure. The statement that the volume varies inversely as the pressure is called *Boyle's Law* and may be expressed algebraically in various forms, such as

$$V \propto \frac{1}{P}, \text{ or } VP = \text{constant},$$

or, if V be the volume at pressure P , the volume V_1 when the pressure is P_1 will be such that

$$V_1 P_1 = VP, \text{ or } V_1 = V \frac{P}{P_1}.*$$

It is evident that if any three of the four quantities are given, the remaining one may be calculated. Pressure may be measured in atmospheres, or it may be measured in pounds per square inch, or it may be measured by the height of a column of mercury, since a liquid exerts a pressure pro-

* It is evident that these three forms mean the same thing, because $V \propto \frac{1}{P}$ means that as the volume increases the pressure diminishes in the same ratio, and *vice versa*. Since the one factor increases exactly in the same ratio as the other factor decreases, the product of the two must always remain constant; and since this is so *always*, it must be true in the particular case where the volume changes from V to V_1 owing to the change of pressure from P to P_1 .

portional to its height. This last method is the most common in chemical work. Atmospheric pressure is ordinarily taken as equal to the pressure which is exerted by a column of mercury 30 inches or 760 mm. high. A pressure of 36.5 inches is therefore more than an atmosphere, and a pressure of 700 mm. is less than an atmosphere. We usually say the gas is under a pressure of so many millimetres.

Problem. — If a quantity of oxygen has a volume of 15 litres at a pressure of 760 mm., what would be its volume under a pressure of 800 mm.? (The full form of expression is, “under a pressure equal to that exerted by a column of mercury 760 mm. high or 800 mm. high,” but the shorter form is usually employed.)

$$\text{Here } V = 15 \quad P = 760 \quad P_1 = 800$$

$$\text{Therefore } V_1 = 15 \times \frac{760}{800} = 14.25 \text{ litres.}$$

In the calculation one does not need to trouble with the formula, but merely ask oneself whether the volume will be greater or less under the new conditions. If the volume of the oxygen is 15 litres

at 760 mm. pressure, it is evident that it will be less at a pressure of 800 mm. in the ratio of $\frac{760}{800} : 1$; the volume then at 800 mm. will be $15 \times \frac{760}{800}$.

Problem. — If the volume of a quantity of hydrogen is 25 litres with a pressure of 720 mm., what pressure will the gas have when the volume is 30 litres?

Here it is evident that the pressure will be less, since the gas is allowed to expand. The pressure will therefore be

$$720 \times \frac{25}{30} = 600 \text{ mm.}$$

Problem. — What volume must carbon monoxide have had at a pressure of 650 mm. if its volume is 18 litres at a pressure of 500 mm.?

Evidently the volume must have been less at 650 mm. than at 500 mm., so that we have

$$18 \times \frac{500}{650} = 13.84 \text{ litres.}$$

EFFECT OF TEMPERATURE

The volume of a gas is also affected by the temperature, becoming greater as the temperature rises, and less as the temperature falls.

The volume is proportional to the temperature, provided we measure the temperature in a certain way.

It is hardly to be expected that we could use the ordinary thermometric scales, however, because the zero in the centigrade and Réaumur scales is fixed merely by the temperature at which water *happens* to freeze, and in the Fahrenheit scale the zero is still more accidental. In all of these scales we have temperatures *below* zero, which shows that the scales are arbitrary.¹

The law that governs the change of volume with temperature could be determined by taking a long glass tube closed at one end, and graduated from the closed end toward the open end. Suppose the tube graduated into 500 equal parts. When the whole tube and the contained air is at 0°C ., insert a small globule of mercury, and by making a passage for the enclosed air by means of a platinum wire passed through the mercury, cause the latter to move down the tube till it reaches the 273 mark. The mercury now shuts in a volume of air which occupies 273 divisions of the tube, the pressure being that of the atmosphere (if the weight of the mercury is negli-

¹ See Appendix C.

gible, or if the tube be held horizontally) and the temperature being 0° C.

If the tube be heated till the temperature is 1° C., the mercury will be driven outward till it reaches the mark 274, where it will remain so long as the temperature stays at 1° C. If the tube be heated to 2° C., the mercury will stand at the mark 275; at 10° C., the volume of the enclosed air will be 283, the mercury standing at the mark 283. At the temperature 100° C. the volume occupied by the air will be 373 divisions, the mercury standing at the mark 373. When the temperature reaches 227° C., the mercury will be just driven out from the tube, the air having expanded to fill the 500 divisions.

On the other hand, if the tube had been cooled down to -10° C., the volume of the air would have been found to be 263 divisions; if cooled down to -25° C., the volume would have been 248 divisions. In general, for every degree rise or fall of temperature, the air which occupied the volume of 273 divisions at 0° C. expands or contracts through one division in the tube. If this law holds to the very lowest temperatures, it follows that at -200° C. the volume of the air would be 73; at -250° C. the

volume would be 23; and at -273° C. the volume would be reduced to zero. This temperature is called the absolute zero of the air thermometer; and if temperatures are measured from this zero instead of from the artificial zeros of the ordinary thermometers, the volume of the air is proportional to its temperature. This is usually called *Charles's Law*, and is expressed in the following form:

If the pressure remain constant, the volume of air, or any gas, is proportional to the temperature measured from the absolute zero.

The zero of the ordinary centigrade thermometer is 273° above the absolute zero, and therefore whenever temperatures are given in degrees centigrade, 273 degrees must be added in order to arrive at the absolute temperature. If T represent the absolute temperature, Charles's Law may be expressed by the formula

$$V \propto T, \text{ or } \frac{V}{T} = \text{constant};$$

or if V be the volume at temperature T , the volume V_1 when the temperature is T_1 will be such that

$$\frac{V_1}{T_1} = \frac{V}{T}, \text{ or } V_1 = V \frac{T_1}{T}$$

Problem. — If the volume of a quantity of carbon monoxide at 0° C. is 18 litres, what will be its volume at 25° C.?

0° C. = 273° absolute temperature,

25° C. = $273 + 25 = 298^{\circ}$ absolute temperature ;

therefore, $T = 273, \quad T_1 = 298,$

and hence $V_1 = 18 \times \frac{298}{273} = 19.64$ litres.

Just as in the case of pressures, instead of following the formula slavishly, we may ask ourselves, will the volume be greater or less under the new conditions than under the old? In this case, we see the volume must be greater, therefore we multiply 18, the original volume, by $\frac{298}{273}$. This common sense way of looking at the question will always prevent mistakes.

Problem. — What must the temperature be so that the gas which occupies a volume of 15 litres at 20° C. will occupy a volume of 16.5 litres? The temperature, 20° C., is $273 + 20 = 293^{\circ}$ absolute, therefore $T = 293$. The new temperature must evidently be greater than this because the gas expands from 15 litres to 16.5 litres. Therefore

$$T_1 = 293 \times \frac{16.5}{15} = 322.3^{\circ} \text{ absolute} = 49^{\circ} 3 \text{ C.}$$

It is evident that the pressure and temperature of a gas may change simultaneously, and it is necessary to be able to calculate the volume under these circumstances.

This is done by a combination of *Boyle's Law* and *Charles's Law*.

Boyle's Law gives $VP = \text{const.}$

Charles's Law gives $\frac{V}{T} = \text{const.}$

These two combined give

$$\frac{VP}{T} = \text{const.}, \text{ or } \frac{VP}{T} = \frac{V_1P_1}{T_1}$$

where V , P , and T are the original volume, pressure, and absolute temperature, and V_1 , P_1 , and T_1 are the final volume, pressure, and temperature. If any *five* of these values are given, the *sixth* may be calculated.

[NOTE.—If the mathematics given above is not clear, the following proof may be read:

Let V , P , and T be the original volume, pressure, and absolute temperature of the gas V_1 , P_1 , T_1 , the final volume, pressure, and absolute temperature. Let us assume that the volume changes, first owing to change of pressure from P to P_1 , the

temperature remaining constant at T . Call the volume, under these new circumstances, v ; then by Boyle's Law

$$v = V \frac{P}{P_1}$$

Let now the temperature change from T to T_1 ; the volume will change from v to V_1 because V_1 is the volume that the gas occupies when both pressure and temperature are changed.

By Charles's Law $V_1 = v \frac{T_1}{T} = V \frac{P}{P_1} \times \frac{T_1}{T}$

or
$$\frac{VP}{T} = \frac{V_1 P_1}{T_1}$$

Problem. — The quantity of chlorine which occupies a volume of 12 litres, at 720 mm. and 10° C. has the pressure changed to 780 mm. and the temperature to 20° C. What is the new volume?

Here $V = 12$ $P = 720$ $P_1 = 780$

$T = 273 + 10 = 283$ $T_1 = 273 + 20 = 293$

Therefore, by applying the formula, we find

$$V_1 = 12 \times \frac{720}{780} \times \frac{293}{283} = 11.46 \text{ litres.}$$

In working such examples, instead of following the formula slavishly, we may arrive at the correct arrangement of the factors by a little consideration of the conditions. This may be seen in the following

Problem.—At what temperature must a gas be, so that its volume will be 15 litres when the pressure is 800 mm., if its volume is 17.5 litres when its temperature is 100° C., and the pressure 700 mm.?

The temperature 100° C. = 273 + 100 = 373° absolute; we have now to consider what the new temperature will be.

The temperature of the gas when its volume is 15 litres would be *less* than when its volume was 17.5 litres (other things being equal). Therefore, if the volume alone be considered, the temperature would be

$$373 \times \frac{15}{17.5}$$

But the gas in the final condition is to be under greater pressure than at the beginning, and therefore would require a *higher* temperature if the volume had remained constant, therefore we must multiply by $\frac{800}{700}$, which is the ratio of the two pressures.

$$\text{Therefore } T_1 = 373 \times \frac{15}{17.5} \times \frac{800}{700} = 365^\circ.4$$

$$365^\circ.4 - 273^\circ = 92^\circ.4 \text{ C.}$$

EXAMPLES

1. If a quantity of nitrogen under 900 mm. pressure at 20° C. occupies a volume of 300 c.c., what volume will it occupy at 100° under 600 mm. pressure? (Cornell Univ., September, 1895.)

Ans. 573 c.c.

2. What would be the volume under standard conditions of a mass of oxygen whose volume is 60 c.c. at 40° C. under a pressure of 750 mm. of mercury? (Cornell Univ., December, 1897.)

Ans. 51.67 c.c.

3. If 1000 c.c. of chlorine at 40° C. stand in a tube over mercury, the level within the tube being 30 mm. above that without, and the barometric pressure being 750 mm., what would be the volume of the gas under standard conditions? (Cornell Univ., September, 1896.)

Since the level of mercury in the tube is 30 mm. above that without, the pressure is $750 - 30 = 720 \text{ mm.}$

Ans. 826.4 c.c.

4. If 2000 c.c. of nitrogen at 27° C. stand in a eudiometer over mercury, the level within the tube being 30 mm. below that without, and the barometric pressure being 750 mm., what would be the volume of the gas under standard conditions? (Cornell Univ., December, 1896.)

Pressure in the tube is $750 + 30 = 780 \text{ mm.}$

Ans. 1868 c.c.

5. If 1250 c.c. of nitrogen at 37° C. stand in a eudiometer over mercury, the level within the tube being 28 mm. above that without, and the barometric pressure being 747 mm., what would be the volume of the gas under standard conditions? *Ans.* 1041 c.c.

If the gas had been standing over water instead of mercury, the pressure in the tube would have been $\left(747 - \frac{28}{13.6}\right)$ mm., since 1 mm. of mercury exerts the same pressure as 13.6 mm. of water.

6. If a quantity of hydrogen occupies 500 c.c. in a tube over mercury, the level within the tube being 40 mm. below that without, the temperature being 20° C., and the barometric pressure 730 mm., what volume will it occupy at 25° C. if the barometric pressure is 750 mm. and the level within the tube is 30 mm. above that without? (Cornell Univ., September, 1898.) *Ans.* 544 c.c.

7. If a quantity of air occupy 500 c.c. in a tube over mercury, the level within the tube being 70 mm. above that without, the temperature being 40° C. and the barometric pressure 740 mm., what volume will it occupy at 20° C., the barometric pressure being 720 mm. and the level within the tube 25 mm. below that without? (Cornell Univ., September, 1897.) *Ans.* 421 c.c.

8. 1.041 litres of hydrogen, measured under standard conditions, is placed in a tube over mercury, the temperature being 37° C. If the volume of the gas is now 1250 c.c., at

what height must the mercury be if the barometric pressure is 755 mm.? *Ans.* 36 mm.

9. If 1868 c.c. of air under normal conditions expand to 2 litres and the level of the mercury inside the tube is 40 mm. below that without, the barometer standing at 740 mm., what must be the temperature? *Ans.* 27° C.

10. If a quantity of moist nitrogen has a volume 25 c.c. at a pressure of 750 mm. and temperature 16° C., what would be its volume when dried, the temperature remaining the same, but the pressure changing to 700 mm.? The pressure of water vapour at 16° C. is 13.5 mm. (see Appendix F); therefore the pressure of the nitrogen alone is

$$750 - 13.5 = 736.5 \text{ mm.}, \text{ and } 25 \times \frac{736.5}{700} = 26.3 \text{ c.c. } \textit{Ans.}$$

11. If 60 c.c. of dry oxygen at 25° C. has enough water put in to saturate the gas, what will be the volume of the moist gas, the pressure remaining at the atmospheric pressure, 750 mm.? If the gas were not allowed to expand, its pressure would become 750 + 23.5; therefore, if allowed to expand so that the pressure will remain the same, its volume must increase to $60 \times \frac{773.5}{750} = 61.9 \text{ c.c.}$

12. What volume would a quantity of air, when dried and measured over mercury, under standard conditions, have, if it occupied a volume of 100 c.c. measured over water, and fully saturated with aqueous vapour, the height of the water in the tube being 27.2 cm., the temperature being 20° C., and the barometer height 750 mm.?

27.2 cm. of water equals 2 cm. or 20 mm. of mercury; therefore the pressure of the moist air is 730, and of the dry air 712.5, since the pressure of the water vapour is 17.5 mm. (nearly).

The required volume is therefore

$$100 \times \frac{712.5}{760} \times \frac{273}{293} = 87.36 \text{ c.c.}$$

13. If a glass tube one square centimetre in cross-section be filled with mercury and inverted over a mercury trough, dry air passed in till the mercury stands at a division of the tube 20 cm. from the closed end, and 30 mm. above the mercury outside, the barometer being 750 mm. and the temperature 20° C., what would be the volume of the air under standard conditions? (The mean coefficient of expansion of mercury between 0° C. and 30° C. is 0.00018143.)

This question evidently involves making a correction for the expansion of mercury, otherwise the data would not be given. The barometer reading will be higher than it would be if the mercury were at 0°, and so will be the column of mercury in the tube. The pressure on the gas will not therefore be exactly 750 - 30 = 720 mm., but a less number for mercury at 0° would not have so great a height. The coefficient of expansion of mercury being 0.00018143, means that the expansion of each millimetre is that amount for every degree rise in temperature, and therefore 0.0036286 for 20°, and a millimetre length at 0° would become 1.0036286 mm. at 20°. A column of mer-

cury 720 mm. long at 20° would therefore be $\frac{720}{1.0036286} = 717.4$ mm. long at 0° . 717.4 mm. is therefore the actual pressure of the gas, and the problem resolves itself into a calculation of the volume of a gas at 0° and 760 mm., its volume being 20 c.c. at 20° and 717.4 mm. *Ans.* 17.6 c.c.

14. What is the actual pressure on the gas in a tube, the level of mercury inside and outside the tube being the same when the barometer reads 760 mm. at 25° C.?

Ans. 756.6.

CHAPTER V

CALCULATIONS INVOLVING WEIGHT AND VOLUME

THE formula of a substance always denotes a certain definite *weight* of that substance, for instance, NH_3 denotes a weight of ammonia 17; it may be pounds or tons or ounces or grammes or kilogrammes. In the same way CO_2 denotes a weight 44, of carbon dioxide, and HCl denotes a weight of 36.5 of hydrochloric acid.

But it is quite evident that this definite *weight* of ammonia will have a definite fixed *volume*, if the gas be measured always at the same temperature and pressure, so that NH_3 represents a certain definite *volume*.

17 pounds of ammonia will occupy a certain definite number of cubic feet when measured at 0°C . and 760 mm. pressure; 17 tons of ammonia will occupy a larger volume under the same conditions, but 17 tons of ammonia will occupy the same volume tomorrow as it does to-day, provided the pressure and temperature remain the same.

In chemical calculations we do not ordinarily use pounds or tons as the unit of weight, nor cubic feet as the unit of volume, but grammes as the unit of weight, and litres as the unit of volume.

17 *grammes* of ammonia at 0° C. and 760 mm. occupy the volume 22.4 *litres* (more exactly 22.253 litres), and the formula NH_3 represents 22.4 *litres* of ammonia at the standard temperature and pressure, quite as readily as it represents 17 *grammes* of ammonia.

In the same manner 44 *grammes* of carbon dioxide, represented by the formula CO_2 , occupy a certain definite volume at the standard temperature 0° C. and 760 mm. This volume is 22.4 *litres*; so also 36.5 *grammes* of hydrochloric acid, represented by the formula HCl , occupy a certain definite volume at the standard temperature and pressure. This volume is 22.4 *litres*.

In general, though the formulæ of different gases represent different *weights*, they always represent the same *volume* at the standard temperature and pressure, and this volume is 22.4 *litres*. This is sometimes called the gramme-molecular volume, but so far as calculations are concerned, it need be con-

sidered only as the volume which is occupied by the formula weight in *grammes*, quite independently of the existence or non-existence of molecules.

Now *two* grammes of hydrogen occupy the volume 22.4 litres at the standard temperature and pressure; therefore if the formula of hydrogen is to represent this fact, it must be written H_2 , for H represents only *one* gramme of hydrogen.

In the same way *thirty-two* grammes of oxygen occupy the volume 22.4 litres, and if the formula of oxygen is to represent this fact, it must be written O_2 , since O represents only *sixteen* grammes.

On the other hand, 200 grammes of mercury vapour, measured at the standard temperature and pressure, would occupy 22.4 litres; therefore if the formula of mercury is to represent this fact, it must be written Hg, since Hg represents 200 grammes.¹

Still further: 124 grammes of phosphorus, when volatilized, occupy a volume corresponding to 22.4

¹ Of course mercury vapour cannot be made to exert a pressure of 760 mm. at 0° C., but if heated till it boils it would have a pressure of 760 mm. (the pressure of the atmosphere), and the volume of 200 grammes at that temperature would be the same as that of 32 grammes of oxygen at that temperature, and 32 grammes of oxygen at the *standard* temperature and pressure has the volume 22.4 litres.

litres, and therefore if the formula of phosphorus is to represent this fact, it must be written P_4 , since P represents only 31 grammes.

✓ Sulphur a little above its boiling point has a volume such that its formula should be S_8 ; at a very high temperature it is represented by the formula S_2 .

The formula of a gas must always represent a volume 22.4 litres at the standard temperature and pressure.

H_2 represents 2 grammes of hydrogen and occupies a volume 22.4 litres

O_2	"	32	"	oxygen	"	"	22.4	"
N_2	"	28	"	nitrogen	"	"	22.4	"
Cl_2	"	71	"	chlorine	"	"	22.4	"
O_3	"	48	"	ozone	"	"	22.4	"
P_4	"	124	"	phosphorus	"	"	22.4	"
As_4	"	300	"	arsenic	"	"	22.4	"
Hg	"	200	"	mercury	"	"	22.4	"
HCl	"	36.5	"	hydrochloric acid	"	"	22.4	"
CO	"	28	"	carbon monoxide	"	"	22.4	"
CO_2	"	44	"	carbon dioxide	"	"	22.4	"
CH_4	"	16	"	methane	"	"	22.4	"
C_2H_2	"	26	"	acetylene	"	"	22.4	"
C_6H_6	"	78	"	benzol	"	"	22.4	"
C_2H_6O	"	46	"	alcohol	"	"	22.4	"

The relative weight of the different gases can easily be seen from the above table. For instance, chlorine is $\frac{71}{32}$ times as heavy as oxygen, while carbon monoxide has the same density as nitrogen. Air,

which is made up of oxygen and nitrogen, has a density lying between them, being nearer that of nitrogen, since this element forms the larger portion of the atmosphere. 22.4 litres of air weigh 28.8 grammes. The specific gravity of any of the gases (that is, its density compared with air) is therefore obtained by dividing its formula weight by 28.8. Thus arsenic vapour is more than 10 times as heavy as air; that is, its specific gravity is greater than 10.

Acetylene and benzol have the same percentage composition which could be represented by the formula CH ; but if this were the formula of either of them, 13 grammes would occupy the volume 22.4 litres. Such is not the case, however: 26 grammes of acetylene occupy the volume 22.4 litres, therefore its formula is C_2H_2 ; and 78 grammes of benzol vapour occupy the volume 22.4 litres, and therefore C_6H_6 is the formula for benzol. There is abundant additional evidence in favour of these formulæ, but for the purpose of calculation nothing more is required.

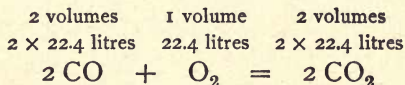
Facts similar to the ones given above caused Avogadro to make the statement in 1811 that equal volumes of gases at the same temperature and pressure contain equal numbers of molecules, and this

statement is usually called *Avogadro's Law*. It was neglected for a long time, because chemists did not have a clear conception of the facts at the foundation of it, and the facts known were not so numerous or varied as at present.

So far as concerns calculations Avogadro's Law might be expressed: The formula weight in grammes, of a gas measured at 0° C. and 760 mm., occupies a volume of 22.4 litres.

Problem. — What volume of carbon dioxide is got from the combustion of 10 litres of carbon monoxide, and what volume of oxygen is required?

The necessary equation is

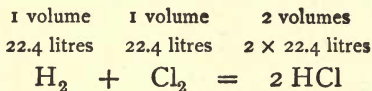


(It is convenient to write weights beneath the formulæ and volumes above.)

The equation shows that the volume of the carbon dioxide is exactly the same as that of the monoxide, and that the volume of the oxygen is half as great; and, therefore, in the case given, 10 litres of carbon dioxide would be produced, and 5 litres of oxygen would be required for the combustion.

Problem. — What volume of hydrochloric acid is obtained when 6 litres of hydrogen unite with chlorine?

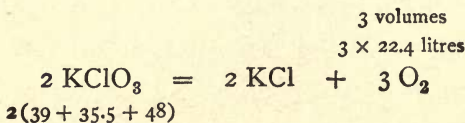
The equation is



The volume of the hydrochloric acid is therefore double that of the hydrogen; therefore, in the case given, 12 litres of hydrochloric acid would be obtained.

Since the formula represents *weight* as well as *volume*, the *weight* of *one* substance might be given, and the *volume* of *another* required, or *vice versa*. (It is of course to be remembered that the volume of *gases only* can enter into the problem.)

Problem. — What volume of oxygen at the normal temperature and pressure can be obtained from 10 grammes of potassium chlorate? The equation is



showing that 245 grammes of chlorate yield $3 \times 22.4 = 67.2$ litres of oxygen. Therefore, 10 grammes of chlorate will yield

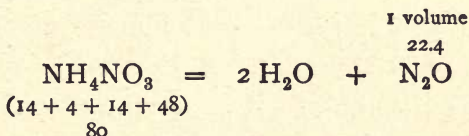
$$67.2 \times \frac{10}{245} = 2.74 \text{ litres.}$$

We now see why we should not write the equation in the form $\text{KClO}_3 = \text{KCl} + \text{O}_3$. This would mean that when 122.5 grammes of potassium chlorate are heated, 22.4 litres of *ozone* are obtained, which is not true.

Nor should it be written $\text{KClO}_3 = \text{KCl} + 3 \text{O}$, because O_2 and not O represents the formula weight of oxygen *corresponding to the standard volume*.

Problem. — What weight of ammonium nitrate will provide 10 litres of nitrous oxide at the normal temperature and pressure (0°C . and 760 mm.)?

From the equation



it is seen that 22.4 litres of nitrous oxide are obtained from 80 grammes of ammonium nitrate;

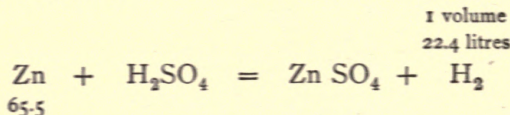
therefore, 10 litres of nitrous oxide are obtained from

$$80 \times \frac{10}{22.4} = 35.71 \text{ grammes of ammonium nitrate.}$$

Since ammonium nitrate is a solid, its volume cannot be calculated.

Problem. — What volume of hydrogen measured at 0° C. and 700 mm. can be obtained by the action of sulphuric acid on 10 grammes of zinc?

The equation



shows that 65.5 grammes of zinc yield 22.4 litres of hydrogen at the standard temperature and pressure, 0° C. and 760 mm.; therefore 10 grammes of zinc will under these conditions yield

$$22.4 \times \frac{10}{65.5} = 3.42 \text{ litres.}$$

In the problem the temperature is the standard temperature, but the pressure is not the standard pressure, so that a correction must be made for the pressure. Since the pressure, 700 mm., in the

example is less than the normal pressure, the volume must be greater than that calculated above. The volume will, therefore, be

$$3.42 \times \frac{760}{800} = 3.71 \text{ litres.}$$

Problem. — What weight of copper is required to produce 15 litres of nitric oxide at 800 mm. and 20° C.?

Since equations give the relation between weight and volume at the standard pressure and temperature, it is necessary first of all to calculate the volume of the nitric oxide at this *normal pressure and temperature*.

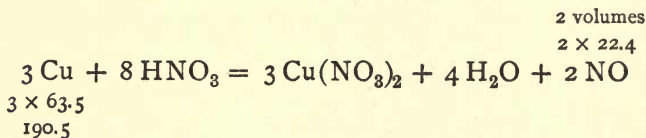
The normal (or standard) *pressure*, 760 mm., is less than that at which the gas is measured, namely, 800 mm.; and therefore the volume at 760 mm. will be $\frac{800}{760}$ times as great.

The standard *temperature* is lower, and on that account the volume would be less. The normal (or standard) temperature is 273° absolute temperature, while that at which the gas is measured is $273 + 20 = 293^\circ$ absolute, and therefore the volume at the normal temperature (temperature alone being considered) is $\frac{273}{293}$ times as great. When

change of pressure and change of temperature are both considered, we have therefore

$$\text{volume} = 15 \times \frac{800}{760} \times \frac{273}{293} = 14.71 \text{ litres.}$$

To arrive at the weight of copper necessary to produce this volume of nitric oxide the equation



is used, and shows that to provide $2 \times 22.4 = 44.8$ litres of nitric oxide 190.5 grammes of copper are required; therefore to produce 14.71 litres of nitric oxide

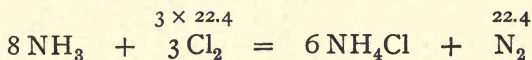
$$190.5 \times \frac{14.71}{44.8} = 62.52 \text{ grammes of copper are required.}$$

Problem. — What volume of nitrogen, measured at 20°C. and 750 mm., would be obtained by the action of ammonia on 300 c.c. (cubic centimetres) of chlorine measured at 15°C. and 735 mm.?

This corresponds to a possible change of temperature and pressure in a laboratory from one time of measuring a gas to another. A cubic centimetre is $\frac{1}{1000}$ of a litre, but as we are dealing with volumes merely, the problem is to be worked out in the same

way as though we were dealing with litres, but the answer obtained is in cubic centimetres, not in litres.

The equation to represent the reaction is



and shows that *three times* 22.4 litres of chlorine yield 22.4 litres of nitrogen at the normal temperature and pressure; or *three times* 22.4 c.c. of chlorine will yield 22.4 c.c. of nitrogen; or, in general, the volume of the chlorine is *three times* that of the nitrogen produced by it.

Therefore 300 c.c. of chlorine will yield $\frac{300}{3} = 100$ c.c. of nitrogen if the two are measured at the *same* temperature and pressure, since all gases are *equally* affected by changes in temperature and pressure, and the same relationship that holds at the normal temperature and pressure will hold at any other. We have then to determine what volume will be occupied by a quantity of nitrogen at 20° C. and 750 mm. if its volume is 100 c.c. at 15° C. and 735 mm.

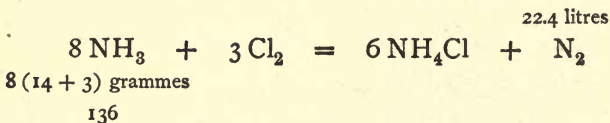
$$\begin{array}{ll} V = 100 & T = 273 + 15 = 288^\circ & T_1 = 273 + 20 = 293^\circ \\ & P = 735 & P_1 = 750 \end{array}$$

$$\text{therefore } V_1 = 100 \times \frac{293}{288} \times \frac{735}{750} = 99.77 \text{ c.c.}$$

The increase in pressure is nearly counterbalanced by the rise in temperature.

Problem. — What *weight* of ammonia would be required in the last problem?

Here we must remember that equations, as we have learned to look upon them, show the relationship between *grammes* and *litres* at 0° C. and 760 mm.



shows that 136 grammes of ammonia are required to produce 22.4 litres of nitrogen at 0° C. and 760 mm. But since a cubic centimetre is $\frac{1}{1000}$ of a litre, $\frac{136}{1000}$ gramme or 0.136 gramme or 136 milligrammes of ammonia would be required to produce 22.4 c.c. of nitrogen measured at 0° C. and 760 mm. But the problem asks how much ammonia is required to produce 100 c.c. of nitrogen measured at 15° C. and 735 mm.; therefore we must find out what this volume will become at 0° C. and 760 mm.

It will evidently be less because the temperature is less; and less also because the pressure is greater.

We have therefore

$$\text{volume} = 100 \times \frac{273}{288} \times \frac{735}{760} = 91.68 \text{ c.c.}$$

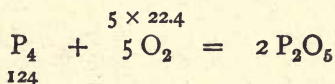
Our problem is ultimately reduced to the question: What weight of ammonia is required to produce 91.68 c.c. of nitrogen when 136 mg. of ammonia produce 22.4 c.c. of nitrogen?

The answer is evidently

$$136 \times \frac{91.68}{22.4} = 556.5 \text{ mg.} = 0.5565 \text{ gramme.}$$

Problem. — At what temperature is the oxygen measured if 10 litres of it, at a pressure of 740 mm., is sufficient for the complete combustion of 10 grammes of phosphorus?

The equation



shows that 124 grammes of phosphorus require 112 litres of oxygen at 0° C. and 760 mm.

Therefore 10 grammes of phosphorus require

$$112 \times \frac{10}{124} = 9.04 \text{ litres.}$$

The question resolves itself into: At what temperature will 9.04 litres of oxygen (measured at

the normal temperature and pressure) expand to 10 litres, its pressure being reduced to 740 mm.?

Since the volume is to increase, the temperature should on that account be higher, but since the *pressure* is to be lessened, so high a temperature would not be required as would otherwise be the case.

The fraction giving the volume factor is therefore greater than unity, and the fraction giving the pressure factor is less than unity; therefore

$$T_1 = 273 \times \frac{10}{9.04} \times \frac{740}{760} = 294.5 = 21^\circ.5 \text{ C.}$$

It is evident that questions involving the use of two or three equations may arise in calculations of volumes as well as in calculations of weights, but they introduce no new principles and need not be further discussed.

EXAMPLES

1. 250 c.c. of oxygen at 10° C. and 756 mm. Find the volume at 0° C. and 760 mm. (Mason Science Coll., 1887.)

Ans. 240 c.c.

2. Find the amount in grammes of 2500 c.c. of sulphur dioxide measured at 20° and 760 mm. (Mason Coll., 1887.)

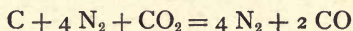
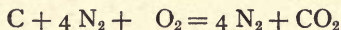
Ans. 6.65 grammes.

3. Calculate the weight of 100 litres of hydrogen sulphide measured at 27° C. and 740 mm. (Lond. Matric., June, 1892.) *Ans.* 134.6 grammes.

4. What volume of sulphuretted hydrogen, measured at 0° C. and 760 mm. pressure, can be obtained from 10 grammes of ferrous sulphide? (Edin. Univ., 1st Professional Med., 1871.) *Ans.* 2.55 litres.

5. What volume, in litres, of oxygen, measured at 740 mm. pressure and 27° C. temperature, can be obtained from 54 grammes of mercuric oxide? (Edin., 1st Professional, 1871.) *Ans.* 3.16 litres.

6. State the relations of volume in the gases involved in the following equations :



(Columbia Univ., 1895, 1st year, 2d term.)

7. A piece of pure marble, weighing 20 grammes, is strongly ignited in a large porcelain crucible. Required the name and weight of the compound which remains behind, and the name and volume in cubic centimetres at 20° C. and 740 mm. mercurial pressure of the gas which escapes. (Princeton Univ., 1896.)

Lime = 11.2 grammes ; carbon dioxide = 4938 c.c.

8. What volume of oxygen, when burned with hydrogen, will yield 40 litres of water vapour under the initial conditions of temperature and pressure? *Ans.* 20 litres.

Solve by inspection. (Cornell Univ., September, 1897.)

9. What volume of olefiant gas would be equal in weight to 10 litres of marsh gas? (Lond. Matric., January, 1889.)

Ans. $5\frac{5}{7}$ litres.

10. How many cubic centimetres of hydrogen can 9.2 grammes of sodium liberate from water, the barometer standing at 710 mm. and the thermometer at 12° C.? (Edin. Univ., 1st Professional, 1889.)

Ans. 5.00 litres = 5000 c.c.

11. How many litres of nitrous oxide, measured at 700 mm. pressure and 15° C. temperature, can be obtained by the decomposition of 100 grammes of ammonium nitrate? (Edin. Univ., 1st Professional, 1871.) *Ans.* 32.07 litres.

12. How many cubic centimetres of hydrogen, measured at 20° C. and 750 mm., will be obtained by dissolving 3.25 grammes of pure zinc in an acid? (Mason Coll., 1882.)

Ans. 1.216 litres = 1216 c.c.

13. Calculate the volume of vapour measured at 100° C. that would be given by 5 c.c. of bromine, the specific gravity of the liquid being 2.96. (Mason Coll., 1886.)

Weight of bromine = $5 \times 2.96 = 14.8$ grammes ;
therefore, volume required = 2.83 litres.

14. What weight of ammonium nitrate must be decomposed under a barometric pressure of 740 mm. at 20° C. to generate sufficient nitrous oxide to fill a balloon holding 200 litres? (Cornell Univ., June, 1896.) *Ans.* 648 grammes.

15. What volume of carbon dioxide will result from the

combustion of 20 litres of carbon monoxide? (Solve without using combining weights.) (Cornell Univ., March, 1898.) *Ans.* 20 litres.

16. Explain why 28.88 multiplied by the density of a gas gives its molecular weight. (Cornell Univ., 1898.)

Molecular weight is what we have called formula weight.

17. (a) Find the molecular weight of the gas whose density is 1.524.

(b) Find the density of the gas whose molecular formula is C_2H_4 .

(c) A litre of nitrous oxide weighs 1.97 grammes; find its molecular weight. (Cornell Univ., 1898.)

(a) Density is compared to air, therefore the formula weight = $28.8 \times 1.524 = 43.9$.

(b) $\frac{28}{28.8} = 0.973$.

(c) $1.97 \times 22.4 = 44.1$.

18. What volume of chlorine at normal temperature and pressure would be required (a) to combine with 10 litres of olefiant gas; (b) to decompose 10 litres of sulphuretted hydrogen liberating the sulphur; (c) to decompose 10 grammes of potassium iodide? (London Matric., June, 1889.) (a) 10 litres; (b) 10 litres; (c) 0.675 litre.

19. How many litres of oxygen, measured at $15^\circ C$. and 750 mm. pressure, are required for the complete combustion of 100 grammes of marsh gas? (Edin. Univ., 1st Professional, 1890.) *Ans.* 299.3 litres.

20. What volume in litres, of oxygen measured at 730 mm. and 10° C., can be obtained from 1 kilogramme of pyrolusite, containing 80% of peroxide of manganese? (Edin. Univ., 1st Professional, 1873.) *Ans.* 74.1 litres.

21. What volume of sulphurous acid gas, measured at 740 mm. pressure and 15° C. temperature, can be obtained by burning 10 grammes of sulphur? (Edin. Univ., 1872.)
Ans. 7.57 litres.

22. (a) Find the density of the gas whose molecular formula is C_2N_2 .
(b) Find the weight of a litre of hydrochloric acid.
(c) 1 litre of a gas weighs 1.25 grammes under standard conditions; find its molecular weight. (Cornell Univ., September, 1896.)

Ans. (a) 1.807; (b) 1.629 grammes; (c) 27.9.

23. How many litres of dry atmospheric air at 740 mm. pressure and 15° C. temperature are required to burn completely 1 litre of olefiant gas at the same temperature and pressure, and what is the weight of carbonic anhydride and of water produced? (Edin. Univ., 1870.)

Take air as containing 21% of oxygen. *Ans.* $14\frac{2}{7}$ litres air.
Weight of carbonic anhydride

$$88 \times \frac{1}{22.4} \times \frac{740}{760} \times \frac{273}{288} = 3.63 \text{ grammes.}$$

Weight of water = 1.486 grammes.

24. What volume of air at 15° C. and 750 mm. would be required to burn 10 litres of marsh gas measured at the normal temperature and pressure? (Assume air contains 20.5% of oxygen.) (Mason Coll., 1885.) *Ans.* 104.1 litres.

25. 50 c.c. of marsh gas are mixed with 600 c.c. of air and exploded. What will be the composition and volume of the residual gas, the measurements being made throughout at normal temperature and pressure? (The Yorkshire Coll., 1896.) *Ans.* 476 c.c. nitrogen; 24 c.c. oxygen; 50 c.c. carbon dioxide.

26. What volume will 9 grammes of water occupy measured in the form of vapour at 273° C. and under 380 mm. pressure? (Aberdeen Univ., Sci. and Med., 1897.) *Ans.* 44.8 litres.

27. What volume of gaseous ammonia, measured at 15° C. and under 380 mm. pressure, may be obtained from 20 grammes of ammonium chloride? (Aberdeen Univ., Sci. and Med., 1898.) *Ans.* 17.66 litres.

28. Calculate the weight of 10 litres of air, measured at 0° C. and 760 mm. pressure, containing 21% of oxygen and 79% of nitrogen. (Lond. Matric., June, 1888.)

$$\frac{21}{100} \times 32 + \frac{79}{100} \times 28 = 28.84 \text{ grammes in } 22.4 \text{ litres.}$$

$$\frac{10}{22.4} \times 28.84 = 12.88 \text{ grammes. } \textit{Ans.}$$

29. If hydrogen were passed over 100 grammes of heated copper oxide as long as action took place, what would be the quantities of the resulting substances, and what volume of the gas measured at the standard temperature and pressure would be needed to complete the change? (London Matric., June, 1893.)

Ans. Copper = 79.9 grammes; water = 22.65 grammes; hydrogen = 28.2 litres.

30. A cubic metre of steam measured at 110°C ., and under standard pressure, is condensed to water at 4°C .; what would be the bulk of the water, and what volume of hydrogen (at 0°C . and 760 mm.) would afford such a quantity of water when burned? (London Matric., January, 1894.) 1 c.c. of water at 4°C . = 1 gramme.

Ans. 573 c.c. water; 713 litres hydrogen.

31. 17 grammes of a mixture of potassium chlorate and manganese dioxide gave 3 litres of oxygen at 20°C . and 760 mm.; calculate the percentage of potassium chlorate in the mixture. (The Yorkshire Coll., 1896.)

Ans. 60%.

32. What volume of air at 15°C . and 740 mm. would be necessary for the combustion of 10 grammes of cyanogen gas? (The Yorkshire Coll., 1895.) Assume air to contain 20.5% oxygen.

Ans. 45.5 litres.

33. A spark is passed through a mixture of 750 c.c. of hydrogen and 250 c.c. of oxygen, both at the temperature of 100°C . What will be the resulting volume measured at 100°C .? (The Yorkshire Coll., 1890.)

Ans. 750 c.c. consisting of 500 c.c. water vapour and 250 c.c. hydrogen.

34. What would be the weight of hydrogen obtained from 7 grammes of oil of vitriol containing 98.2% of sulphuric acid? What volume would it occupy at 19°C . and 744 mm.? (Queen's Coll., Galway, 1897.)

Ans. 0.1402 gramme; 1.71 litres.

35. 0.2 gramme of iron wire by solution in acid gave 83.7 c.c. of hydrogen at 12°C . and 750 mm. What percentage of pure iron is contained in the sample? (Mason Coll.) *Ans.* 98.9%.

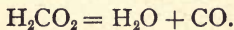
36. A blue flame is often seen at the top of a coke or charcoal fire. To what substance is it due and how is the flame formed? Suppose that the coke used contained 90% of carbon and it was entirely converted into this substance, how much coke would be needed to make 10,000 litres measured at 15°C . and 750 mm.? (London Matric.)

Ans. 5570 grammes.

37. 50 grammes of crystallized oxalic acid ($\text{H}_2\text{C}_2\text{O}_4, 2\text{H}_2\text{O}$) are decomposed by heating with strong sulphuric acid. What is the composition of the gas evolved, and what volume (in c.c.) will it occupy if measured at 15°C . and 748 mm.? (Mason Coll.)

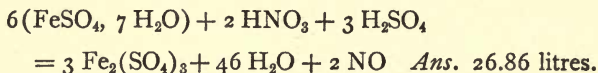
Ans. Equal volume of carbon monoxide and carbon dioxide. Total volume = 19,052 c.c.

38. What volume of gas measured at standard temperature and pressure would be evolved by the action of concentrated sulphuric acid: (a) on 10 grammes of oxalic, (b) on 10 grammes of formic acid, both anhydrous? (Aberdeen Univ., 1891.) Anhydrous oxalic acid has the formula $\text{C}_2\text{H}_2\text{O}_4$, and formic acid the formula H_2CO_2 , and the latter decomposes according to the equation



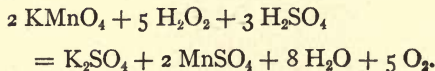
Ans. (a) 4.98 litres; (b) 4.86 litres.

39. What volume of nitric oxide gas measured at 0°C . and 760 mm. can be obtained by acting on 1000 grammes of ferrous sulphate ($\text{FeSO}_4, 7 \text{H}_2\text{O}$) with the necessary quantities of nitric and sulphuric acids? (Edin. Univ., 1889.) The equation is



40. How many litres of nitric oxide gas measured at 750 mm. and 10°C . can be obtained by treating 100 grammes of ferrous chloride (FeCl_2) with excess of nitric acid? (Edin. Univ., 1871.) *Ans.* 6.17 litres.

41. A solution of potassium permanganate containing 31.6 grammes per litre was added to 20 c.c. of a solution of hydrogen peroxide acidulated with sulphuric acid till the colour was no longer destroyed. 35.8 c.c. of the permanganate solution were used. What amount of peroxide was present per 100 c.c. of the solution? It was observed that gas was given off. What volume would 100 c.c. of peroxide solution have afforded? (London Univ. B. Sc., 1893.) The equation is



The weight of permanganate in 35.8 c.c.

$$= \frac{35.8}{1000} \times 31.6 = 1.133 \text{ grammes.}$$

Weight of peroxide in 20 c.c.

$$= 1.133 \times \frac{170}{316} = 0.608 \text{ gramme.}$$

Weight of peroxide in 100 c.c.

$$= 0.608 \times 5 = 3.04 \text{ grammes.}$$

$$\text{Volume of oxygen} = \frac{3.04}{170} \times 112 = 2.005 \text{ litres.}$$

42. 0.2 gramme of a dyad metal when dissolved in hydrochloric acid evolved 83.81 c.c. of hydrogen measured in the moist state under a pressure of 750 mm. and at 15° C. Calculate the atomic weight of the metal, vapour pressure of water at 15° C. being 12.7 mm. (London Univ., Intermediate Exam. in Science, 1895.) The formula of the chloride is RCl_2 , where R stands for metal, since the latter is dyad. The pressure of hydrogen is $750 - 12.7 = 737.3$ mm. The volume of hydrogen under standard conditions

$$= 83.81 \times \frac{273}{288} \times \frac{737.3}{760} = 77.19.$$

The problem reduces itself to: If 0.2 gramme of the metal yield 77.19 c.c. of hydrogen, how much will yield 22,400 c.c.? *Ans.* 58.1, which is the atomic weight.

43. What volume of air would be required for the complete combustion of 100 litres of a gas containing hydrogen 46%, marsh gas 40%, olefiant gas 14% by volume? (London Int. Sci., 1889.)

Ans. Of air containing 20% oxygen, 725 litres.

44. One gramme of a metal *A* when dissolved in acid liberates 930 c.c. of hydrogen measured at 18° C. and 750 mm.; also 1 gramme of a metal *B* when dissolved

in nitric acid yields 1.65 grammes of nitrate. From these data calculate the equivalent of each metal. (London Univ. Int. Sci., 1890.)

Ans. A 13; B 95.4.

45. What volume of air containing 21% of oxygen measured at 20° C. and 760 mm. will be required to burn completely 10 grammes of pure carbon? (London Univ., Prelim. Sci. Med., January, 1890.)

Ans. 95.4 litres.

46. What weight of potassium bichromate would be required to provide enough chlorine to combine with 20 litres of ethylene measured at 20° C. and 770 mm.?

Ans. 82.6 grammes.

47. How much calcium carbide would be required to produce enough acetylene to yield, on combustion, 14 litres of carbon dioxide measured at 15° C. and 740 mm., and what volume of oxygen at the same temperature and pressure would be needed?

Ans. 18.5 grammes calcium carbide; 17.5 litres of oxygen.

48. What volume of oxygen measured at 10° C. and 780 mm. pressure would be required for the complete combustion of the marsh gas obtainable from 20.5 grammes of sodium acetate?

Ans. 11.3 litres.

CHAPTER VI

CALCULATIONS IN VOLUMETRIC ANALYSIS

It is not within the scope of this little book to treat at all fully the subject of volumetric analysis, but a few examples may be given to illustrate the principles set forth in the preceding chapters.

In volumetric analysis, solutions are used whose strength is known. In some cases the strength may follow no regular system. These may be called *arbitrary* solutions, or *unsystematic* solutions. For example, a potassium permanganate solution might be made up, somewhat at haphazard, and be found by testing to have such a strength that 1 c.c. of it will oxidize 0.01324 gramme of iron from the ferrous to the ferric condition; in other words, change the amount of ferrous sulphate, containing that much iron, into ferric sulphate (sufficient sulphuric acid being assumed present).

It will readily be seen that if a gramme of ore is taken, each c.c. of the permanganate used will repre-

sent 1.324% of iron (for it is 0.01324 gramme in one gramme).

To simplify calculations, solutions which may be called *even-number* solutions are sometimes used. For example, if a permanganate solution is prepared so that each cubic centimetre equals 0.0100 gramme of iron, then, if 1 gramme of ore require 31.2 c.c. of this solution, the amount of iron is seen at once to be 31.2%. Even-number solutions are the most convenient ones, so far as saving of calculation goes, in cases where only a single substance is to be determined with the volumetric solution; but where several substances are to be determined with the solution, the latter will be an even-number solution for not more than one of the substances. For instance, a solution of permanganate which would give percentages in 1 gramme of iron ore, would not give percentages of manganese in 1 gramme of a manganese ore, or percentages of oxalic acid in an impure oxalate.

When the solution is used for varied purposes, calculations are somewhat simplified by the use of normal solutions, or solutions which bear some simple numerical relation to the latter, such as $\frac{1}{4}$ normal, $\frac{1}{10}$ normal (decinormal), or $\frac{1}{100}$ normal (centinormal).

This saving in calculation is usually accomplished by taking a weight of the substance for analysis which bears a simple relation to the standard, or formula, weight of the substance sought. For example, if 0.56 gramme of iron ore is taken, each cubic centimetre of a decinormal potassium bichromate solution will correspond to 1% of iron, or, if 0.80 gramme of ore is taken, will correspond to 1% of ferric oxide (Fe_2O_3).

The statement just made involves a distinct definition of the term "normal," and since the term is used in different senses by different chemists, it is always necessary, in working problems involving the term, to make sure that the definition required by the problem is clearly borne in mind.

According to one definition, the normal solution contains the standard, or molecular, weight in grammes, of the substance in 1 litre; according to another definition, the normal solution contains the gramme *equivalent* of the substance per litre; while, according to a third definition, the normal solution contains the *hydrogen equivalent in grammes* per litre. According to any of the definitions the standard, or normal, solution of hydrochloric acid

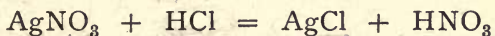
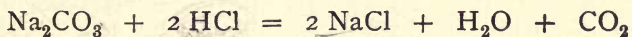
would have a weight of 36.5 grammes of pure hydrochloric acid in the volume of 1 litre. According to the first definition, normal sulphuric acid solution would have 98 grammes of sulphuric acid (H_2SO_4) in the litre. But 98 grammes of pure sulphuric acid would neutralize twice as much caustic potash as 36.5 grammes of pure hydrochloric acid, so that, if the acid solutions are to be equivalent, the sulphuric acid should contain only 49 grammes of sulphuric acid, which is the normal solution according to the second definition.

The potassium permanganate solution, which has the formula weight KMnO_4 of salt in a litre, is capable of oxidizing *five* times the amount of hydrogen contained in the normal solution of hydrochloric acid, and, according to the third definition, the normal solution would contain $\frac{15.8}{5}$ grammes ($\frac{1}{5} \text{KMnO}_4$) per litre; that is, has one-fifth the concentration of the normal solution, according to the first definition.

The second and third definitions amount to the same thing in most cases; but since there may be ambiguity, in some instances, as to the signification of "equivalent weight," the term "normal solution" will, in this chapter, be used in the sense of the third definition.

Problem.—If 1 c.c. of hydrochloric acid neutralizes 0.0106 gramme of sodium carbonate, what weight of silver chloride will be precipitated when 1 c.c. is added to excess of silver nitrate solution? (Yale Scientific School, 1898.)

The equations are



which show that two formula weights of silver chloride correspond to one formula weight of sodium carbonate.

2×143.5 grammes of silver chloride are precipitated by the acid which is neutralized by 106 grammes of sodium carbonate, or 0.0287 gramme of silver chloride corresponds to 0.0106 gramme of sodium carbonate, and would therefore be precipitated by 1 c.c. of the given hydrochloric acid solution.

Problem.— If 1 c.c. acid \equiv 1.25 c.c. alkali solution, and if to standardize 50 c.c. acid solution, 10 c.c. alkali solution and 0.25 gramme of sodium carbonate are used; 1 c.c. alkali is equivalent to what weight of actual hydrochloric acid (HCl)?

1 c.c. acid \equiv what weight of nitrogen (by Kjeldahl)?
(Yale Scientific School, 1898.)

10 c.c. alkali solution \equiv 8 c.c. acid, so that 42 c.c. acid solution are neutralized by 0.25 gramme of sodium carbonate, or 1 c.c. by $\frac{0.25}{42}$ gramme.

By the equation above, 73 grammes of hydrochloric acid neutralize 106 grammes of sodium carbonate, and hence to neutralize $\frac{0.25}{42}$ gramme of sodium carbonate, $73 \times \frac{0.25}{42 \times 106} = 0.004099$ gramme of actual hydrochloric acid is necessary.

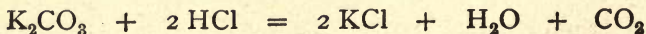
By Kjeldahl's method nitrogen is converted into ammonia, and each standard weight of nitrogen, namely 14, corresponds to the standard weight of hydrochloric acid, 36.5.

Therefore, the nitrogen is

$$0.004099 \times \frac{14}{36.5} = 0.001572 \text{ gramme.}$$

Problem.—What volume of centinormal acid would be required to neutralize 0.005 gramme of potassium carbonate (K_2CO_3)?

The equation



shows that 138 grammes of potassium carbonate are neutralized by twice the amount of hydrochloric acid contained in a litre of normal strength; and as, according to the definition of *normal* which we adopt, all acids of normal strength are equivalent, 138 grammes of potassium carbonate would be neutralized by 2 litres of any acid of normal strength, or by 200 litres of acid of centinormal strength.

To neutralize 0.005 gramme of carbonate,

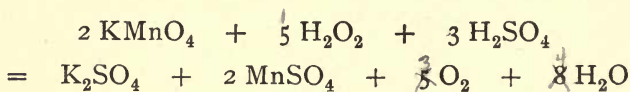
$$200 \times \frac{0.005}{138} = 0.007242 \text{ litre} = 7.24 \text{ c.c.}^1$$

Problem.—How many cubic centimetres of a decinormal permanganate solution would be required to just produce a colour in 100 c.c. of a centinormal

¹ While the above is the *exact* interpretation of the equation, it is more common to express the fact in a slightly different form, and instead of saying that the formula weight of potassium carbonate requires *twice* the formula weight of hydrochloric acid, to say that *half* the formula weight of potassium carbonate requires the formula weight of hydrochloric acid, or that since the formula weight of potassium carbonate contains twice the standard (or atomic) weight of potassium, *half* of its formula (or molecular) weight must be taken to be equivalent to the formula (or molecular) weight of hydrochloric acid which contains the standard (or atomic) weight of hydrogen.

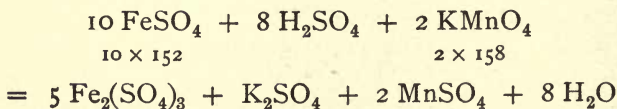
solution of peroxide of hydrogen to which sulphuric acid is added?

The equation



represents the fact that the oxygen comes equally from the permanganate and from the peroxide, and therefore the normal solutions are equivalent; and, therefore, 10 c.c. of a decinormal permanganate is equal to 100 c.c. of a centinormal peroxide solution.

Problem.—What must be the strength of a ferrous sulphate solution such that 100 c.c. of it will be sufficient just to decolourize 20 c.c. of a permanganate solution containing 15.8 grammes of salt per litre?



From this equation it is evident that 2×158 grammes of permanganate oxidize 10×152 grammes of ferrous sulphate; and, therefore, if the permanganate could oxidize an equal volume of the ferrous sulphate solution, the latter must contain 5×152

grammes of ferrous sulphate for every 158 grammes of potassium permanganate in the permanganate solution. In the problem we have assumed the ferrous sulphate solution to be only one-fifth as strong, and therefore it must contain 15.2 grammes of sulphate for every 158 grammes of permanganate, or 15.2 grammes per litre. If we were dealing with crystallized ferrous sulphate ($\text{FeSO}_4 \cdot 7 \text{H}_2\text{O}$), the amount required would be 27.8. It is important to notice this, since the salt is usually weighed out in the crystalline form.

Problem.—What weight of iron is contained in 1 c.c. of the ferrous sulphate solution in the last question, and what per cent of iron is there in an ore if 13.6 c.c. of the permanganate solution be used for 1.42 grammes of ore?

The iron is $\frac{5.6}{15.2}$ of the ferrous sulphate; therefore, since there is 15.2 grammes ferrous sulphate per litre, there would be 5.6 grammes of iron per litre, or 0.0056 gramme per 1 c.c.

The permanganate solution in the given case is capable of oxidizing *five* times its volume of a ferrous sulphate solution containing this quantity of

iron; therefore, 13.6 c.c. of permanganate solution would oxidize $13.6 \times 5 = 68$ c.c. of ferrous sulphate, which contains $68 \times 0.0056 = 0.3808$ gramme of iron.

1.42 grammes of ore contains 0.3808 gramme of iron, or 26.82 %.

Problem.—What weight of ore must be taken so that the number of cubic centimetres of the permanganate solution above will represent the percentage in iron?

1 c.c. of the permanganate is equivalent to $0.0056 \times 5 = 0.028$ gramme of iron, and if this is equal to 1 %, the total ore must be 2.8 grammes.

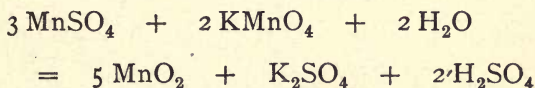
Problem.—What must be the strength of a permanganate solution if the burette reading in cubic centimetres gives the percentage of iron direct when 0.7 gramme of ore is taken?

In this case 1 c.c. of permanganate must correspond to 0.007 gramme of iron, since if the substance were pure iron, 100 c.c. of the permanganate would be necessary for the 0.7 gramme; and since 15.8 grammes of the permanganate correspond to $5.6 \times 5 = 28$ grammes of iron, the permanganate solution required by the problem must contain

$0.7 \times \frac{15.8}{28} = 0.395$ gramme permanganate per 100 c.c.,
or 3.95 grammes per litre.

Problem. — 1 c.c. of a permanganate solution is equivalent to (will oxidize) 0.014 gramme of iron; 1 c.c. is equivalent to what weight of manganese in a hot neutral solution (Volhard's method)? (Yale Scientific School, 1898.)

This reaction goes according to the equation



The equation which represents the reaction of permanganate with a ferrous salt shows that 2KMnO_4 oxidizes 10 Fe; while this equation shows that 2KMnO_4 oxidizes 3 Mn. Therefore the amount of permanganate which would oxidize $10 \times 56 = 560$ grammes of iron would oxidize $3 \times 55 = 165$ grammes of manganese.

The answer to the problem is therefore $\frac{165}{560} \times 0.014 = 0.0041$ gramme of manganese.

Problem. — If 10 c.c. of a permanganate solution are heated with hydrochloric acid, the liquid evap-

orated with excess of sulphuric acid, the residue taken up with water, neutralized with zinc oxide, and boiled, how many cubic centimetres of the same permanganate solution will be required to precipitate the manganese? (Yale Scientific School, 1899.)

The question gives the details of the Volhard process, and the equation in the last problem shows that there is $\frac{2}{3}$ as much manganese in the permanganate as in the manganese sulphate, and therefore, if a given quantity of permanganate is changed to manganese sulphate, it will require $\frac{2}{3}$ as much permanganate to oxidize it again to the condition of dioxide; hence in this case $6\frac{2}{3}$ c.c.

Problem. — A solution of permanganate containing 6.32 grammes per litre :

(a) What is its strength in terms of Fe_2O_3 ?

(b) What amount of iron ore must be weighed out so that each cubic centimetre used will represent one per cent of iron (Fe)?

(c) What is the strength of this solution against manganese by Volhard's method? (Columbia Univ.)

Ans. (a) 0.0160 gramme of Fe_2O_3 per cubic centimetre.

(b) 1.12 grammes.

(c) 0.0033 gramme manganese per cubic centimetre.

Problem. — If 0.5 gramme of iron is dissolved, without oxidation, in water containing 5 grammes of sulphuric acid (H_2SO_4), and the requisite amount of permanganate is run in, what weight of free acid will the solution contain? (Yale Scientific School, 1899.)

By examination of the equations it will be seen that in order to dissolve the iron and to complete the reaction with permanganate, $18 \text{H}_2\text{SO}_4$ is required for 10Fe ; therefore, for 0.5 gramme of iron $\frac{18 \times 98}{10 \times 56} \times 0.5$ gramme of sulphuric acid are necessary; therefore the free acid is

$$5 - \left(\frac{18 \times 98}{10 \times 56} \times 0.5 \right) = 3.425 \text{ grammes.}$$

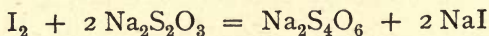
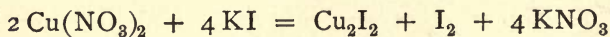
Problem. — Two grammes of ore containing arsenic were treated according to Pearce's method, and the silver in the silver arsenate determined by titration with ammonium sulphocyanate; the

amount was 27.9 c.c., the strength of solution 1 c.c. = 0.007 gramme of silver. What was the percentage of arsenic?

Pearce's method consists in obtaining neutral sodium arsenate, precipitating the arsenic acid as silver arsenate, collecting the precipitate and dissolving in nitric acid, and titrating with ammonium sulphocyanate solution.

In the problem given, the silver used was 27.9 \times 0.0007 = 0.1953 gramme, and from the formula of the precipitate Ag_3AsO_4 , $3 \times 108 = 324$ parts of silver correspond to 75 parts of arsenic, therefore the arsenic = $0.1953 \times \frac{75}{324} = 0.0452$ gramme in 2 grammes of ore; that is, 2.26%.

Problem. — How much crystallized sodium thio-sulphate ($\text{Na}_2\text{S}_2\text{O}_3, 5\text{H}_2\text{O}$) must be dissolved in water and diluted to 1 litre to give a solution whose strength is 1 c.c. = 0.015 gramme of copper?



that is, one standard weight of copper 63.5 corresponds to one formula weight of thiosulphate

($\text{Na}_2\text{S}_2\text{O}_3, 5 \text{H}_2\text{O}$) 248; therefore, $0.015 \times \frac{248}{63.5} = 0.05859$ gramme of thiosulphate per cubic centimetre, or 58.59 grammes per litre.

Problem. — What weight of crystallized sodium thiosulphate will make 1000 c.c. of a solution, 1 c.c. of which will be equivalent to 0.0008 gramme of oxygen (available), by Bunsen's method of distilling a higher oxide of manganese with hydrochloric acid and collecting the chlorine in potassium iodide solution? (Yale Scientific School, 1898.)

0.0008 gramme of oxygen corresponds to 0.00355 gramme of chlorine, and this to 0.0127 gramme of iodine, and by the equation above 0.0127 gramme iodine corresponds to 0.0248 gramme of thiosulphate crystals; therefore, 1000 c.c. should contain 24.8 grammes of sodium thiosulphate crystals.

Problem. — We have a rich copper matte and decide to take 0.5 gramme for analysis. How much sodium thiosulphate ($\text{Na}_2\text{S}_2\text{O}_3$) per litre will give a solution such that 1 c.c. will equal 2% of copper? (Columbia Univ.)

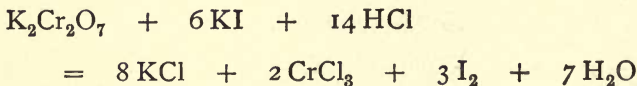
From the equations above, 63.5 grammes of cop-

per require 158 grammes of thiosulphate; hence 0.5 gramme of copper would require $\frac{158}{63.5} \times 0.5 = 1.2442$ grammes of thiosulphate, which must be contained in 50 c.c., since if the ore were pure copper, 50 c.c. of the thiosulphate solution must be added, according to the conditions of the problem.

There must therefore be $1.2442 \times 20 = 24.884$ grammes per litre.

Problem. — 1 c.c. of a potassium bichromate solution contains x grammes of the pure salt. 1 c.c. will liberate what weight of iodine from an acid solution of potassium iodide? 1 c.c. will be equivalent to what weight of iron?

The equation



shows that 294 grammes of bichromate yield 762 grammes of iodine; hence $\frac{762}{294}x$ is the weight of iodine.

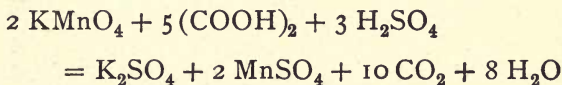
A consideration of the equation will show that there are $16 \times 3 = 48$ grammes of oxygen useful for oxidizing purposes in 294 grammes of bichro-

mate; or, as is usually said, there is 3 O (available) which will oxidize 6 Fe from ferrous to ferric condition; hence the weight of iron is $\frac{6 \times 56}{294}x$.

Problem. — Suppose 1 c.c. of permanganate solution is equivalent to 0.028 gramme of iron. What will be the strength of the oxalic acid solution, such that it will just decolourize an equal volume of the permanganate?

Since 158 grammes of permanganate oxidizes $56 \times 5 = 280$ grammes of iron, the solution of permanganate in the example must contain 15.8 grammes per litre.

But from the equation

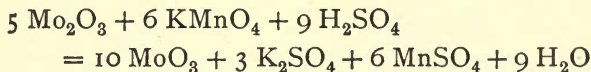


it is evident 2×158 grammes of permanganate oxidize 5×90 grammes of oxalic acid. Therefore, the solution of oxalic acid to be equivalent to the permanganate must contain $\frac{5}{2} \times 9 = 22.5$ grammes oxalic acid per litre.

Problem. — Compare the phosphorus standard with the iron standard for potassium permanganate.

When phosphorus is precipitated as yellow ammonium phospho-molybdate, the ratio is one standard weight of phosphorus (P) to 12 standard weights of molybdic acid (MoO_3), and the weight of the phosphorus is $\frac{31}{1728}$ that of the molybdic acid.

The molybdic acid is then reduced to the compound represented by the formula Mo_2O_3 , which is oxidized by permanganate according to the equation



so that 6 KMnO_4 corresponds to 10 MoO_3 .

But we saw that 6 KMnO_4 corresponds to 30 Fe, so that MoO_3 corresponds to 3 Fe, or 144 grammes of molybdic acid correspond to 168 grammes of iron.

But 31 grammes of phosphorus correspond to 1728 grammes of molybdic acid; therefore to 1728 $\times \frac{168}{144}$ grammes of iron.

Therefore,

$$\begin{aligned} \text{phosphorus standard} : \text{iron standard} \\ = 31 : 1728 \times \frac{168}{144} = 0.01538 : 1, \end{aligned}$$

which means that, in the titration for phosphorus, 1 c.c. of permanganate solution represents a much smaller amount of phosphorus than it would of iron, in an iron estimation.

Problem. — If a sample of iron contains 97% pure iron, and if it requires as much of the given permanganate solution in the phosphorus estimation as in the iron estimation, what is the percentage of phosphorus?

$$\frac{31 \times 97 \times 144}{168 \times 1728} = 1.492\%. \text{ Ans.}$$

Problem. — What weight of substance must be weighed out for analysis:

(a) so that 1 c.c. of the decinormal acid will be equivalent to 1% of nitrogen by Kjeldahl?

(b) so that 1 c.c. of the same acid will represent 1% of sodium carbonate (Na_2CO_3)?

(c) 1% of sodium oxide (Na_2O). (Yale Scientific School, 1898.)

(a) 0.14 gramme; (b) 0.53 gramme;

(c) 0.31 gramme.

Problem. — A quantity of caustic potash solution requires 32 c.c. of normal acid solution to neutralize it. What is the weight of potassium hydrate (KOH) in the solution? *Ans.* 1.792 grammes.

Problem. — 5.3 grammes of moist sodium carbonate require 90 c.c. of a normal solution of acid to neutralize it. What is the percentage of water?

Ans. 10%.

Problem. — If a solution of silver nitrate contains 17 mg. of salt per cubic centimetre, how many cubic centimetres of a centinormal potassium chloride solution would be needed to precipitate the silver contained in 9.64 c.c. of the silver nitrate solution?

17 mg. per cubic centimetre is the same as 17 grammes per litre; therefore the silver solution is decinormal, and will therefore require 10 times its volume of the centinormal potassium chloride solution, or 96.4 c.c.

CHAPTER VII

CALCULATION OF FORMULÆ

THE organic chemist very frequently meets the problem of determining what formula to give a substance with which he is dealing. In order to do this, he must, after determining what the constituents of the substance are, find out the relative quantities of these constituents. This really amounts to finding the percentage composition of the substance, and though it is not actually necessary to calculate out the percentage composition, this is usually done, and the chemist sets down the figures representing the percentage composition, and gives the formula that he calculates from these figures.

The constituent elements of the substance are not, in general, separated and weighed, but they are converted into compounds whose composition is already known. For instance, it is not feasible to separate the carbon from alcohol and determine its amount in that way, but it is very easy to burn the alcohol

in such a manner that all the carbon dioxide produced may be collected and weighed. In the same way, hydrogen is weighed as water, chlorine is converted into silver chloride, and sulphur into barium sulphate. When we know the amount of each of these substances produced, there is no difficulty in calculating the amount of the element which we are considering.

Carbon, for instance, is $\frac{12}{44}$ the weight of the carbon dioxide produced by its combustion, hydrogen is $\frac{2}{18}$ the weight of the water, chlorine is $\frac{35.5}{143.5}$ the weight of the silver chloride obtained, and sulphur $\frac{32}{233}$ the weight of the barium sulphate.

Example. — When 1.124 grammes of chloroform are burned, 0.4139 gramme of carbon dioxide and 0.0846 gramme of water are obtained. If the same quantity is treated in the proper way, it yields 4.050 grammes of silver chloride. These are all of the results obtained by actual analysis; it remains for us to see how the formula of chloroform may be deduced from these data.

We know that when 12 grammes of carbon are burned, 44 grammes of carbon dioxide are obtained,

and therefore that the amount of carbon is $\frac{12}{44}$ of the amount of carbon dioxide produced by its combustion. The amount of carbon in 1.124 grammes of chloroform must therefore be

$$0.4139 \times \frac{12}{44} = 0.1127 \text{ gramme.}$$

In the same manner, 2 grammes of hydrogen yield 18 grammes of water, and therefore the amount of hydrogen is $\frac{2}{18}$ of the amount of water produced by the combustion. The amount of hydrogen in 1.124 grammes of chloroform is therefore

$$0.0846 \times \frac{2}{18} = 0.0094 \text{ gramme.}$$

Also 35.5 grammes of chlorine gives 143.5 grammes of silver chloride, and therefore the amount of chlorine is $\frac{35.5}{143.5}$ of the amount of silver chloride. The amount of chlorine in 1.124 grammes of chloroform is therefore $4.050 \times \frac{35.5}{143.5} = 1.002$ grammes.

We know that every standard quantity of carbon, which we represent by the symbol C, weighs 12 times as much as the standard quantity of hydrogen, which we represent by the symbol H; so that if the weight of carbon actually found is divided by 12, and the

weight of the hydrogen by unity, and the quotient is the same, we know that there are just as many standard quantities of carbon as of hydrogen. If the quotient obtained by dividing the weight of carbon by 12 is one-half as great as that obtained by dividing the weight of hydrogen by unity, we know that there are half as many standard quantities of carbon as of hydrogen. If the quotient is twice as great in the first case as in the second, we know that there are twice as many standard quantities of carbon as of hydrogen.

In the same way, if the amount of chlorine is divided by 35.5, the quotient obtained will show how many standard quantities of chlorine, represented by the symbol Cl, there are for every standard quantity of carbon or of hydrogen.

In the case of the numbers we have found for chloroform, we observe that

$$\frac{0.1127}{12} = 0.0094 = 0.0094 \times 1$$

$$\frac{0.0094}{1} = 0.0094 = 0.0094 \times 1$$

$$\frac{1.002}{35.5} = 0.0282 = 0.0094 \times 3$$

which gives the ratio of the standard quantities of carbon, hydrogen, and chlorine. The formula for chloroform is therefore CHCl_3 , or some multiple of it such as $\text{C}_2\text{H}_2\text{Cl}_6$, $\text{C}_3\text{H}_3\text{Cl}_6$, etc.

Simple analysis of the substance does not decide between these formulæ, for all that the analysis proves is that for every standard quantity of carbon there is *one* standard quantity of hydrogen and *three* standard quantities of chlorine.

The formula which expresses in the simplest form the composition of a substance is called its *empirical* formula, and this may or may not be the formula that best represents the *standard* quantity of the substance, which is ordinarily called the *molecular* formula.

When a substance is volatile, its vapour density is of very great importance in deciding what formula is best to apply to it. Other considerations are taken into account, but this is the only one with which we are immediately concerned. The vapour density of chloroform shows that its correct formula is CHCl_3 , and not a multiple.

When the same quantity of a substance is used for all determinations, we have seen that the

empirical formula may be arrived at by dividing the *quantity* of each element by the *standard weight* of that element, the quotients obtained showing the relative number of these standard weights. In fact, it is not necessary to calculate how much of each element is present, for we arrive at the same result if we divide the amount of carbon dioxide actually obtained by 44 as if we first find out how much carbon that corresponds to and divide it by 12. So also we may divide the weight of water by 9, since $\frac{1}{9}$ of the water is hydrogen; and in the same way we may divide the amount of silver chloride by 143.5.

But though carbon and hydrogen are always estimated together, chlorine, sulphur, and nitrogen are always estimated in separate experiments, and usually with different amounts of substance. 1.124 grammes of chloroform are far too much to take for an estimation of chlorine, since 4.050 grammes of silver chloride are an inconveniently large amount to deal with.

But though different amounts of substance are taken for different determinations, it is easy to calculate from the data obtained how much of each element is contained in *one* gramme of the sub-

stance, or in 100 grammes; in other words, to find the *percentage* composition. The results of analysis are therefore usually worked up into percentages and put down in that form.

Example.—0.353 gramme of ethyl sulphide by combustion gave 0.692 gramme of carbon dioxide and 0.353 gramme of water. Also, 0.241 gramme of sulphide gave 0.642 gramme of barium sulphate.

It is required to calculate the formula. We have

Weight of carbon dioxide for 1 gramme

$$= 0.692 \times \frac{1000}{353} = 1.959 \text{ grammes.}$$

Weight of water for 1 gramme

$$= 0.353 \times \frac{1000}{353} = 1.000 \text{ gramme.}$$

Weight of barium sulphate for 1 gramme

$$= 0.624 \times \frac{1000}{241} = 2.583 \text{ grammes. } \times$$

Weight of carbon for 1 gramme

$$1.959 \times \frac{12}{44} = 0.5342 = 53.42\%$$

Weight of hydrogen for 1 gramme

$$1.000 \times \frac{2}{18} = 0.1111 = 11.11\%$$

Weight of sulphur for 1 gramme

$$2.583 \times \frac{32}{333} = 0.3554 = 35.54\%$$

100.07

That the percentages add up to 100.07 instead of exactly 100 shows a slight error either in the estimation of the constituents or in the calculations.

To get the formula we have

$$\frac{53.42}{12} = \overset{\text{Ratio}}{4.45} = 1.11 \times 4 \quad \text{C}$$

$$\frac{11.11}{1} = 11.11 = 1.11 \times 10 \quad \text{H}$$

$$\frac{35.54}{32} = 1.11 = 1.11 \times 1 \quad \text{S}$$

Therefore the formula is $\text{C}_4\text{H}_{10}\text{S}$ or some multiple. As a matter of fact, the way in which the substance is produced indicates that the above is the correct formula.

As has been stated, it is not absolutely necessary to *calculate* the percentage of each constituent in the substance, though the data must always be such that the calculation is possible. This may be shown by an example, and we shall choose one in which a nitrogen determination is involved.

When the volume (at a certain temperature and pressure) of nitrogen obtained from a quantity of substance is given, it is easy to calculate its weight

and therefore the weight which would be obtained from 1 gramme of the substance; and the remainder of the calculation is similar to the preceding.

Example. — It is required to calculate the formula of ethylamine from the following data :

I. 0.263 gramme of substance gives 0.515 gramme of carbon dioxide and 0.363 gramme of water.

II. 0.328 gramme produces 109.7 c.c. of nitrogen at 15° C. and 750 mm.

The weight of carbon dioxide produced by 1 gramme is

$$0.515 \times \frac{1000}{263} = 1.955.$$

The weight of water produced by 1 gramme is

$$0.363 \times \frac{1000}{263} = 1.380.$$

The weight of nitrogen produced by 1 gramme is

$$\frac{109.7}{22400} \times 28 \times \frac{273}{288} \times \frac{750}{760} \times \frac{1000}{328} = 0.311 \text{ gramme.}$$

Ratio

$$\frac{1.955}{44} = 0.0445 = 0.022 \times 2 \quad \text{C}$$

$$\frac{1.380}{9} = 0.153 = 0.022 \times 7 \quad \text{H}$$

$$\frac{0.311}{14} = 0.022 = 0.022 \times 1 \quad \text{N}$$

Therefore the formula is C_2H_7N .

The results obtained in actual practice are not so exact as the figures given above. The estimation of carbon is usually too low, and the estimation of hydrogen too high. The formula is chosen which most nearly represents the results of experiment and suits the chemical character of the substance. Then the percentages of the elements are put down as calculated from this formula and side by side, for comparison, the percentages actually obtained.

Example. — I. 0.1520 gramme of a substance gave 0.3352 gramme of carbon dioxide and 0.0708 gramme of water.

II. 0.2071 gramme of the substance gave 64.5 c.c. of nitrogen at $23^{\circ}.5$ C. and 774.5 mm.

	Calculated from formula $C_8H_8N_4$	Found
C	60	60.16
H	5	5.18
N	35	35.60
	<hr/> 100	<hr/> 100.94

So that the formula was probably $C_8H_8N_4$, though the analysis was not very satisfactory. The follow-

ing results are more satisfactory. An analysis of parabromphenyl hydrazin gave these data :

I. 0.234 gramme of substance gave 0.328 gramme of carbon dioxide and 0.082 gramme of water.

II. 0.132 gramme gave 17.5 c.c. of nitrogen measured at 17° C. and 742 mm.

III. 0.1435 gramme gave 0.1435 gramme of silver bromide.

	Calculated from formula $C_6H_7N_2Br$	Found
C	38.50	38.28
H	3.71	3.93
N	14.97	14.94
Br	42.72	42.56
	<hr/> 100.00	<hr/> 99.71

These results are better than those in the last case, not only because the percentages found add up to a number more nearly equal to 100, but because the error in each determination is in the direction which is to be naturally expected.

Sometimes two formulæ are given, and the percentages calculated from them are put side by side with those actually obtained by experiment.

Example. — I. 0.1541 gramme of a substance gave 0.4426 gramme of carbon dioxide and 0.1128 gramme of water.

II. 0.1097 gramme gave 0.3164 gramme of carbon dioxide and 0.0824 gramme of water.

III. 0.3014 gramme gave 36.1 c.c. of nitrogen at 21° C. and 743.5 mm.

	Calculated for formula		Found		
	C_7H_9N	C_6H_7N	I	II	III
C	78.50	77.42	78.22	78.58	
H	8.41	7.53	8.13	8.35	
N	13.09	15.06			13.0

Here the first formula is the better one, as is especially seen in the nitrogen determination.

It must always be borne in mind that the results of analysis do not decide between a formula and any multiple of that formula. This matter can be decided only by other considerations, and among these the vapour density (for any substance that will volatilize) is a very important one.

Somewhat similar calculations are made for inorganic substances. In these cases it is sometimes required to calculate the standard (or atomic) weight

of a metal as well as the formula of the compound. An important point in such determination is the *specific heat* of the element, which, multiplied by the standard weight, gives a product approximately equal to *six*. The vapour density of compounds also is of importance in this connection.

Problems are sometimes set in the calculation of the formulæ of minerals, in which the percentage of each element is given. These problems may be worked in exactly the same way as when the formula of an organic compound is required.

In minerals, however, the constituents vary largely, one metal being replaced in part by another which gives isomorphous compounds. In the case of minerals containing oxygen, such as carbonates and silicates, the metal is usually estimated as oxide, and the percentages given in that way.

The following is an example given in the ordinary form:

CaO	28.4
MgO	12.3
FeO	12.3
MnO	1.9
CO ₂	<u>44.4</u>
	99.3

That the numbers do not add up to exactly 100 is due to the difficulty in making a perfectly accurate analysis.

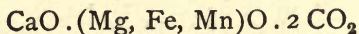
In the same manner as the ratios between the *elements* of organic compounds were calculated, we may calculate the ratios of the oxides. The quantity of calcium oxide must be divided by 56, of magnesium oxide by 40, and so on.

Doing this with the mineral in question, we have:

		Ratio	
Calcium oxide,	28.4%	$\frac{28.4}{56} = 0.507$	
Magnesium oxide,	12.3%	$\frac{12.3}{40} = 0.307$	} 0.504
Ferrous oxide,	12.3%	$\frac{12.3}{72} = 0.170$	
Manganese oxide,	1.9%	$\frac{1.9}{71} = 0.027$	
Carbon dioxide,	44.4%	$\frac{44.4}{44} = 1.009$	

The ratio of the calcium oxide to the magnesium oxide, along with the oxides which replace it isomorphously, is 1 : 1, and to the carbon dioxide 1 : 2.

Therefore the formula may be written



or $\text{Ca}(\text{Mg, Fe, Mn})(\text{CO}_3)_2$; or it may be considered as a mixture of the isomorphous substances, $\text{CaMg}(\text{CO}_3)_2$, $\text{CaFe}(\text{CO}_3)_2$, and $\text{CaMn}(\text{CO}_3)_2$, the relative amounts of these substances being shown by the ratios 307, 170, and 27. If the mineral were pure dolomite, we should have more magnesium oxide, instead of the iron oxide and manganese oxide. It is interesting to calculate the amount of magnesium oxide corresponding to those other oxides, and thus obtain the percentage composition of pure dolomite from the results of this analysis.

The weight of MgO is evidently $\frac{40}{72}$ that of FeO and $\frac{40}{71}$ that of MnO . In the ratios obtained above we have already divided by the denominators of these fractions; hence, to obtain the amounts of MgO , corresponding to the FeO and MnO , we merely need to multiply the ratios by 40.

Doing this we have :

Ratio	
FeO	$0.170 \times 40 = 6.8\%$ MgO equivalent to FeO
MnO	$0.027 \times 40 = 1.1\%$ MgO equivalent to MnO .
	<u>12.3%</u> MgO in analysis.
	20.2% Total MgO .

This amount of magnesium oxide added to the calcium oxide and carbon dioxide does not amount to 100, but to 93; but we may easily calculate it into percentages.

$$\begin{array}{r}
 \text{CaO} \quad 28.4 \div 0.93 = 30.5\% \\
 \text{MgO} \quad 20.2 \div 0.93 = 21.7 \\
 \text{CO}_2 \quad 44.4 \div 0.93 = 47.8 \\
 \hline
 \quad \quad 93. \qquad \qquad \quad 100. \%
 \end{array}$$

and this percentage corresponds with the formula $\text{CaO} \cdot \text{MgO} \cdot 2 \text{CO}_2$ or $\text{CaMg}(\text{CO}_3)_2$.

A sample of pyroxene may be taken as another illustration.

$$\begin{array}{r}
 \text{Silica} \quad \quad \quad 55.40\% ; \quad \frac{55.40}{60} = 0.923 \\
 \text{Ferrous oxide} \quad \quad 2.50\% ; \quad \frac{2.50}{72} = 0.035 \\
 \text{Manganese oxide} \quad 2.83\% ; \quad \frac{2.83}{71} = 0.040 \\
 \text{Magnesium oxide} \quad 22.57\% ; \quad \frac{22.57}{40} = 0.564 \\
 \text{Calcium oxide} \quad \quad 15.70\% ; \quad \frac{15.70}{56} = 0.280
 \end{array} \left. \vphantom{\begin{array}{l} \\ \\ \\ \\ \end{array}} \right\} 0.919$$

Ratio, 1 : 1 ; Formula, $(\text{Mg}, \text{Ca}, \text{Mn}, \text{Fe})\text{O}, \text{SiO}_2$.

In order to show what variations may occur, and how nearly the ratios approach to the ideal, the analyses of different garnets may be given.

Garnets.

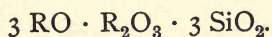
	I	II	III
SiO ₂	38.25%	37.11%	36.65%
Al ₂ O ₃	19.35	5.88	17.50
Fe ₂ O ₃	7.33	—	—
Cr ₂ O ₃	—	22.54	6.20
FeO	—	2.44	4.97
MnO	0.50	—	—
MgO	2.40	1.10	0.81
CaO	31.75	30.34	33.20
	<u>99.58%</u>	<u>99.41%</u>	<u>99.33%</u>

From I. SiO₂ : (Al₂O₃, Fe₂O₃) : (MnO, MgO, CaO)
= 0.637 : 0.235 : 0.634 ;

From II. SiO₂ : (Al₂O₃, Cr₂O₃) : (FeO, MgO, CaO)
= 0.618 : 0.198 : 0.602 ;

From III. SiO₂ : (Al₂O₃, Cr₂O₃) : (FeO, MgO, CaO)
= 0.611 : 0.214 : 0.681 ;

therefore the probable formula for garnet is



Though calculations do not depend upon any theory regarding the constitution of matter, all the facts described find a ready explanation if the existence of atoms is admitted, matter being considered as composed of indivisible particles. In this way it

is seen why the quantity of oxygen united to a given quantity of carbon should be exactly twice as much in carbon dioxide as in carbon monoxide.

The kinetic theory of gases gives support to the idea of molecules and to Avogadro's law. It is not the purpose of this little book, however, to deal with the theoretical side of the subject.

EXAMPLES

1. State concisely how the combining weight of an element, as, for example, nitrogen, can be found from vapour density determinations and analyses. (Cornell Univ., March, 1898.)

Analysis of ammonia shows the volume of the contained hydrogen to be 3 times that of the nitrogen, and this with the vapour density determines the formula NH_3 . The weight of the nitrogen is $4\frac{2}{3}$ that of the hydrogen, therefore the weight represented by the symbol N is 14 times that represented by the symbol H.

2. Alcohol contains

Carbon	52.17%
Oxygen	34.79
Hydrogen	13.04

The specific gravity of its vapour is 1.593 (referred to air); find its molecular weight. (Cornell Univ., June, 1896.)

Ans. $\text{C}_2\text{H}_6\text{O}$.

3. One gramme of acetic acid gave on combustion 1.466 grammes of carbon dioxide and 0.600 of water. The vapour density of acetic acid is 30. Calculate the percentage of carbon, hydrogen, and oxygen; give the empirical and molecular formulæ. (Columbia Univ., May, 1898.)

Ans. Carbon = 40%, hydrogen = 6.66%.

The percentage of oxygen is obtained by subtracting the sum of the carbon and hydrogen from 100, and is 53.34%. Empirical formula CH_2O , but since this formula represents 22.4 litres of vapour as weighing only 30 grammes, that is, only *fifteen* times as much as hydrogen, the molecular formula must be $\text{C}_2\text{H}_4\text{O}_2$, which is *thirty* times as heavy as hydrogen.

4. One gramme of alcohol gave, on combustion, carbon dioxide 1.913, water 1.173. The vapour density of alcohol is 23; calculate the percentage of carbon, hydrogen, and oxygen; give the empirical and molecular formulæ. (Columbia Univ., May, 1898.)

Ans.

Carbon	52.2
Hydrogen	13.0
Oxygen	34.8
Empirical formula	$\text{C}_2\text{H}_6\text{O}$
Molecular formula	$\text{C}_2\text{H}_6\text{O}$

5. Calculate the formula of mellitic acid from the following data :

Carbon	42.1%
Hydrogen	1.7
Oxygen	56.2
	100.0

All the hydrogen can be replaced by a metal. It is hexabasic. (Harvard Univ., 1885.)

The simplest or empirical formula is C_2HO_2 , but since it is hexabasic and all the hydrogens may be replaced by metal, the formula as above given must be multiplied by 6; therefore the molecular formula is $C_{12}H_6O_{12}$.

6. Calculate the atomic weight of molybdenum from the following data :

Percentage composition of chloride

Molybdenum	40.33
Chlorine	59.67
	<hr style="width: 100%; border: 0.5px solid black;"/>
	100.00

Specific heat of molybdenum = 0.064. (Harvard Univ., 1887.)

Since the specific heat multiplied by the atomic weight should give a number approximately equal to 6, the atomic weight of molybdenum should be in the neighbourhood of 94.

But the quantity of the chlorine is approximately $\frac{3}{2}$ as great as the molybdenum, therefore 94 of molybdenum would need 141 of chlorine. But 141 is approximately 4×35.5 , therefore we may assume that the chloride in question has the formula $MoCl_4$.

With this assumption, we calculate from the data —

$$\text{Atomic weight of molybdenum} = 40.33 \times \frac{142}{59.67} = 96$$

7. Determine the atomic weight of glucinum from the following data :

The vapour density of glucinic chloride is 40.2, and it contains 11.7% of glucinum. (Harvard Univ., 1885.)

The vapour density being 40.2, the standard (or molecular) weight is 80.4; and the chlorine must be 71, therefore the glucinum is 9.4 (or some submultiple). This agrees exactly with the analysis given. That 9.4 is more likely correct than any submultiple is proved by other considerations.

8. A metal X forms a volatile chloride containing

$$X = 34.46$$

$$\text{Chlorine} = 65.54$$

The vapour density of the chloride referred to hydrogen is 81.25. The specific heat of the metal is 0.11379. Calculate the atomic weight of X and give the formula of the chloride. (London Univ. Int. Sci., 1893.)

From the specific heat, the atomic weight of X is between 50 and 60, and therefore from the vapour density and a superficial glance at the proportion of the elements in the chloride, it appears that the formula is XCl_3 . Then making use of the exact figures, the atomic weight of X is found to be 56.

9. Calculate the formula of the substance from the following percentage composition :

Silicon 26.27

Calcium 18.43

Magnesium 11.06

Oxygen 44.24

(Sydney Univ., 1894.)

Ans. $\text{CaMgSi}_2\text{O}_6$

10. Two specimens of chromite upon analysis gave the following percentages :

	I	II
Cr ₂ O ₃	55.37%	55.14%
Al ₂ O ₃	13.97	5.75
Fe ₂ O ₃	1.10	12.06
FeO	18.04	18.02
MgO	<u>10.04</u>	<u>9.39</u>
	98.52	100.36

What is the typical formula?

Ans. RO · R₂O₃.

11. What is the formula of the mineral three samples of which gave on analysis :

	I	II	III
S	15.92%	17.83%	19.93%
Ag	52.71	28.79	24.04
Cu	<u>30.95</u>	<u>53.38</u>	<u>53.94</u>
	99.58	100.00	97.91

Ans. (Ag, Cu)₂S.

12. Two samples of erythrite, on analysis, gave the following percentages. What is the formula of the mineral?

	I	II
As ₂ O ₅	38.43%	36.42%
CoO	36.52	23.75
NiO		11.26
FeO	1.01	3.51
CaO		0.42
H ₂ O	24.10	23.52

Ans. 3 RO · As₂O₅ · 8 H₂O.

13. Penfield found by analysis of triphylite the following composition. What is the formula of the mineral?

P_2O_5	44.76
FeO	26.40
MnO	17.84
CaO	0.24
MgO	0.47
Li_2O	9.36
Na_2O	0.35

Ans. $P_2O_5 \cdot 2(Fe, Mn, Ca, Mg)O \cdot (Li_2, Na_2)O$, or chiefly $Li(Fe, Mn)PO_4$.

Miscellaneous Examples

1. What volume of chlorine should be obtained at $20^\circ C$. and 760 mm., by acting on 1 gramme of manganese dioxide with hydrochloric acid? (Univ. of Sydney, 1895.)

Ans. 276.3 c.c.

2. What volume of carbon monoxide, at a temperature $819^\circ C$. and pressure 720 mm., would be required to reduce 1 kilogramme of ferrous oxide to metallic iron? (Univ. of Sydney, 1895.)

Ans. 1313.5 litres.

3. How many litres of oxygen are required for the complete combustion of 2 litres of each of the following: (a) carbon monoxide, (b) methane, (c) ethylene, (d) acetylene? (Univ. of Sydney, 1896.)

Ans. (a) 1 litre; (b) 4 litres; (c) 6 litres; (d) 5 litres.

4. A monobasic organic acid has the empirical formula CH_2O ; 0.296 gramme of its silver salt gave on ignition 0.162 gramme of silver. What is its molecular weight and molecular formula? (Univ. of Sydney, 1896.)

Since the acid is monobasic, the silver salt has the formula AgX , where X stands for all that is not silver, and the acid itself has the formula HX . The molecular weight of the silver salt is therefore $108 \times \frac{296}{162} = 197$; hence the molecular weight of the acid HX is 90, which is three times the weight represented by the empirical formula CH_2O . The molecular formula, therefore, of the acid is $\text{C}_3\text{H}_6\text{O}_3$.

5. What is the result of the action of chlorine on ammonia? How much chlorine would be required to decompose 1.7 grains of ammonia? (McGill Univ. Med. Exam., 1897.)

Ans. 2.66 grains.

6. The composition of a compound is

Barium	46.12
Sulphur	21.54
Oxygen	<u>32.32</u>
	99.98

What is the formula and name of the compound? (First Professional Exam., Glasgow Univ., 1888.)

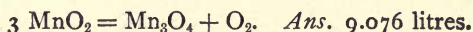
Ans. Barium dithionate; BaS_2O_6 .

7. A substance has the following composition: carbon 10.04%, hydrogen 0.83%, chlorine 89.13%, and its vapour density is 59.75. What is its name and formula? (First Professional Exam., Glasgow, 1888.)

Ans. Chloroform; CHCl_3 .

8. A litre of a mineral water yielded 0.0134 gramme of silver iodide. How much iodine is contained in 100,000 c.c. of the water? (First Professional Exam., Glasgow Univ., 1889.) *Ans.* 0.7241 gramme.

9. How many litres of oxygen, at 12° C. and 750 mm. pressure, can be got by heating 100 grammes of manganese dioxide? (First Professional Exam., Glasgow Univ., 1890.)



10. Calculate the weight of zinc and hydrochloric acid, respectively, which would be required to produce hydrogen to inflate a balloon of 1000 cubic metres capacity, at a temperature of 15° C., and pressure of 760 mm. What would be the bulk of the gas when the barometer had fallen to 730 mm., and the temperature was -6° C.? (First Professional Exam., Glasgow Univ., 1891.)

1 cubic metre = 1000 litres.

Ans. Zinc, 2771.8 kilogrammes; hydrochloric acid, 3089.2 kilogrammes; 965.18 cubic metres.

11. What are the formula and name of the salt having the following percentage composition?

Calcium	38.72
Phosphorus	20.00
Oxygen	41.28

(First Professional Exam., Glasgow Univ., 1892.)

Ans. Tricalcic phosphate; $\text{Ca}_3(\text{PO}_4)_2$.

12. A liquid containing 1 gramme of sodium chloride was added to another containing 2 grammes of silver ni-

trate. Whether did the filtered liquid contain sodium chloride or silver nitrate, and how much? (First Professional Exam., Glasgow Univ., 1892.)

Ans. Sodium chloride; 0.3117 gramme.

13. What volume of hydrogen and oxygen, respectively, could be got from a cubic centimetre of water at its maximum density point? (First Professional Exam., Glasgow Univ., 1892.)

Ans. Hydrogen, 1.244 litres; oxygen, 0.622 litre.

14. To what temperature centigrade would 30 litres of hydrogen measured at 70° F. require to be reduced to occupy 20 litres? (First Professional Exam., Glasgow Univ., 1893.)

70° F. = 21.1° C. *Ans.* — 76.93° C.

15. Calculate what volume of nitrogen, measured at 15° C. and 750 mm., could be obtained from 1 gramme of urea by the action of sodium hypobromite, assuming all the nitrogen to be liberated in the process. (First Professional Exam., Glasgow Univ., 1896.)

It is only necessary for this problem to know the formula of urea, since we are told that all the nitrogen is liberated. Urea has the formula $\text{CO}(\text{NH}_2)_2$. *Ans.* 251.71 c.c.

16. What weights of ammonium chloride and quick lime must be taken in order to produce 2 litres of ammonia—the gas to be measured at 17° C. and 750 mm.? (First Professional Exam., Glasgow Univ., 1897.)

Ans. Ammonium chloride, 4.439 grammes; quick lime, 2.963 grammes.

17. What volume of oxygen gas, measured at 700 mm. pressure and 10° C. temperature, can be obtained from 100 grammes of potassium chlorate? (First Professional Exam., Edin. Univ., 1888.)

Ans. 30.87 litres.

18. How many litres of oxygen, measured at 15° C. and 750 mm., are required for the complete combustion of 100 grammes of marsh gas? (First Professional Exam., Edin. Univ., 1891.)

Ans. 299.3 litres.

19. How many cubic centimetres of carbonic anhydride, measured at 730 mm. and 20° C., would be obtained by the complete combustion of 1 gramme of cane sugar? (First Professional Exam., Edin. Univ., 1891.)

Ans. 878.4 c.c.

20. What would be the weight of the products of the complete combustion of 500 grammes of ethylene, and what would be the volume in litres of the gaseous product measured at 10° C. and 740 mm.? (First Professional Exam., Edin. Univ., 1892.)

Ans. 2214.3 grammes; 851.73 litres.

21. Hydrochloric acid is diluted with water until 100 c.c. of the dilute solution exactly precipitate 0.34 gramme of silver nitrate; how many cubic centimetres of this dilute hydrochloric acid are required exactly to neutralize 0.68 gramme of ammonia? (First Professional Exam., Edin. Univ., March, 1893.)

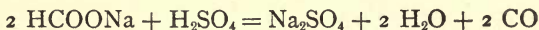
Ans. 2000 c.c.

22. What percentage of iron is contained in pure ferrous carbonate? (First Professional Exam., Edin. Univ., July, 1893.)

Ans. 48.29%.

23. What volume in litres of carbonic oxide, at 760 mm and 0° C., can be obtained from 10 grammes of sodium formate, by the action of strong sulphuric acid? (First Professional Exam., Edin. Univ., 1894.)

The equation representing the reaction is



Ans. 3.294 litres.

24. What volume of nitrogen at standard temperature and pressure can be obtained from 100 grammes of ammonium nitrite? (First Professional Exam., Edin. Univ., 1894.)

Ans. 35 litres.

25. 50 c.c. of a given solution of hydrochloric acid are exactly sufficient to precipitate as silver chloride the whole of the silver from 2 grammes of silver nitrate. What weight of caustic soda would be exactly neutralized by 100 c.c. of this solution? Calculate the result to three places of decimals. (First Professional Exam., Edin. Univ., July, 1894.)

Ans. 0.941 gramme.

26. Calculate to two places of decimals the percentage composition of silver acetate. (First Professional Exam., Edin. Univ., July, 1895.)

Ans. Silver, 64.67% ; carbon, 14.37% ; hydrogen, 1.79% ; oxygen, 19.16%.

27. What weight of metallic zinc is required for the precipitation of 5 grammes of metallic silver from a solution of silver acetate? (First Professional Exam., Edin. Univ., March, 1896.)

Ans. 1.470 grammes.

28. Calculate the percentage composition of urea, to two places of decimals. (First Professional Exam., Edin. Univ., 1896.)

Ans. Carbon, 20.00% ; oxygen, 26.67% ; nitrogen, 46.67% ; hydrogen, 6.66%.

29. What weight in grammes of silver oxide must be taken to obtain, by heating it, 1 litre of oxygen gas measured at 0° C. and 760 mm.? (First Professional Exam., Edin. Univ., July, 1897.)

Ans. 20.72 grammes.

30. What volume in litres of hydrogen, measured at 0° C. and 760 mm. pressure, would be produced by the action of 20 grammes of sodium on water? What would be the volume at 18° C. and 750 mm.? (First Professional Exam., Edin. Univ., March, 1898.)

Ans. 9.739 litres ; 10.517 litres.

APPENDICES

APPENDIX A

THE FRENCH SYSTEM OF MEASURES

THE French standard of *length* is the metre, which is a little more than 39.37 inches. It is divided into tenths, hundredths, and thousandths, called respectively decimetre, centimetre, and millimetre; the Latin prefixes being used for the fractions. Greek prefixes are used to denote multiples of the standard, the most important being the kilometre, which is 1000 metres or 0.6214 mile.

The standard *capacity* is the litre or cubic decimetre, equal to 1.76 pints. It is also subdivided into decilitre, centilitre, and millilitre, but, instead of using these terms, it is more common to use the term cubic centimetre, 1000 of which make a litre.

10 millilitres or 10 c.c. = 1 centilitre

10 centilitres or 100 c.c. = 1 decilitre

10 decilitres or 1000 c.c. = 1 litre

A cubic centimetre of water at the temperature of 4° C. weighs a gramme, which is the standard of *weight*, and is divided into decigrammes, centigrammes, and milligrammes. The weight of a litre of water at 4° C. is 1000 grammes or 1 kilogramme, equal nearly to 2.2 pounds avoirdupois.

APPENDIX B

ARITHMETICAL CALCULATIONS

THE full form of the calculation on page 19 is
96 grammes of oxygen are prepared from 245 grammes of
potassium chlorate.

1 gramme of oxygen is prepared from $245 \times \frac{1}{96}$ gramme
of potassium chlorate.

80 grammes of oxygen are prepared from $245 \times \frac{80}{96}$ gramme
of potassium chlorate.

It should never be necessary for the student to go through all of the steps, however. To prepare 80 grammes of oxygen evidently requires less chlorate than to prepare 96 grammes; and it is almost equally evident that it requires $\frac{80}{96}$ as much. The student can always be kept right in the manipulation of the fractions by asking the simple question whether the answer should be more or less than the number given (by the equation or otherwise), and then by arranging the terms of the fraction so as to obtain the required result. This is really the old Rule of Three expressed in different form, and I should not have thought it necessary to write this appendix, except that I have found by experience that blunders are made by students from whom one might least expect it. The method of solving problems from the common-sense point of view rather than by direct application of formula has been frequently followed in the text, and is the one which is best fitted to prevent slips in the arithmetic.

APPENDIX C

COMPARISON OF THERMOMETRIC SCALES

THERE are two thermometric scales in which the melting point of ice is taken as the zero. These are the Centigrade and Réaumur scales. In the former the boiling point of water is called 100 (whence the name centigrade); in the latter, 80.

In the Fahrenheit scale the distance between the melting point of ice and the boiling point of water is divided into 180 parts; but the melting of ice is not the zero, but is called 32° , and the zero probably marks what Fahrenheit considered the *lowest attainable* temperature.

The method of changing from one scale to the other is so clearly given in Tait's "Heat" that I transcribe it: "If we suppose the same thermometer to have these three separate scales adjusted to it, or (still better) engraved side by side upon the tube, we easily see how to reduce from one scale to the other.

F	0	32	f	212
C	0	c	100	
R	0	r	80	

"For if f, c, r be the various readings of one temperature, it is obvious that

$f - 32$ bears the same ratio to $(212 - 32, \text{ or } 180)$
 that c bears to 100
 and r bears to 80

"Hence
$$\frac{f - 32}{180} = \frac{c}{100} = \frac{r}{80}."$$

APPENDIX D

CALCULATION OR ATOMIC WEIGHTS OF THE MORE
COMMON ELEMENTS

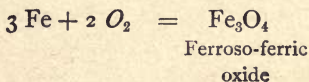
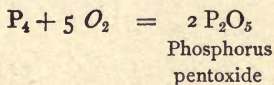
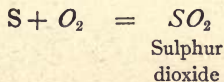
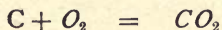
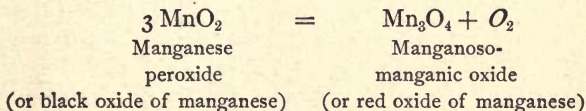
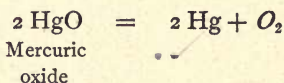
NAME.	SYM- BOL.	WEIGHT.	NAME.	SYM- BOL.	WEIGHT.
Aluminium . . .	Al	27	Iodine	I	127
Antimony . . .	Sb	120	Iron	Fe	56
Arsenic	As	75	Lead	Pb	207
Barium	Ba	137	Magnesium . . .	Mg	24.5
Bismuth	Bi	208	Manganese . . .	Mn	55
Boron	Bo	11	Mercury	Hg	200
Bromine	Br	80	Nickel	Ni	58.5
Cadmium	Cd	112.5	Nitrogen	N	14
Calcium	Ca	40	Oxygen	O	16
Carbon	C	12	Phosphorus . . .	P	31
Chlorine	Cl	35.5	Potassium	K	39
Chromium	Cr	52	Silicon	Si	28.5
Cobalt	Co	59	Silver	Ag	108
Copper	Cu	63.5	Sodium	Na	23
Fluorine	F	19	Strontium	Sr	87.5
Gold	Au	197.5	Sulphur	S	32
Hydrogen	H	1	Tin	Sn	119
			Zinc	Zn	65.5

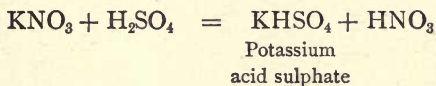
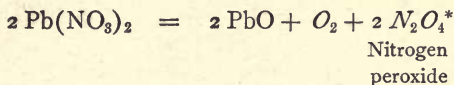
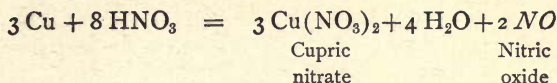
APPENDIX E

EQUATIONS IN FREQUENT USE

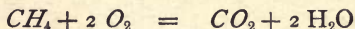
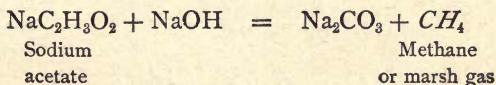
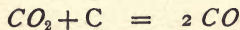
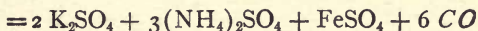
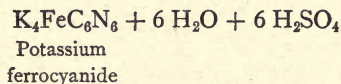
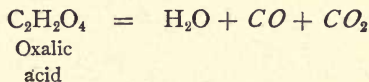
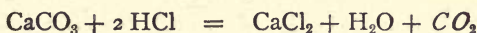
THE following equations are among the most commonly met. Though equations are made to represent the facts as found out by experiment, the beginner often finds it easiest to remember the equation, and to translate it into a verbal expression of the experimental fact. In the following equations *gases* are represented by the italics, and of these *volumes* may be calculated.

OXYGEN

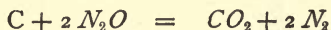
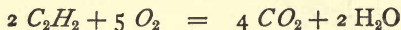
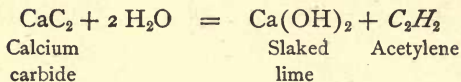




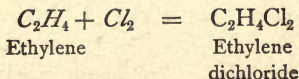
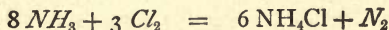
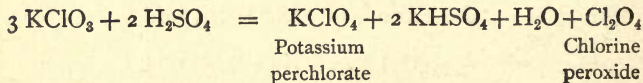
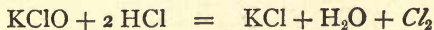
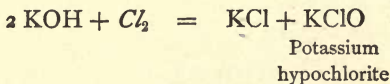
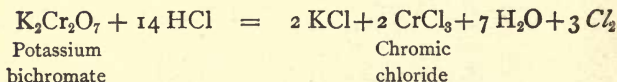
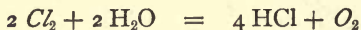
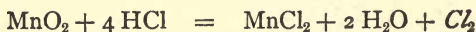
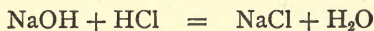
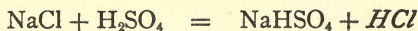
CARBON



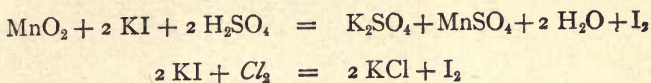
* At about 100° C. the formula of nitrogen peroxide is NO_2 .



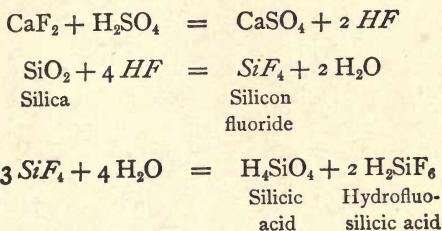
CHLORINE



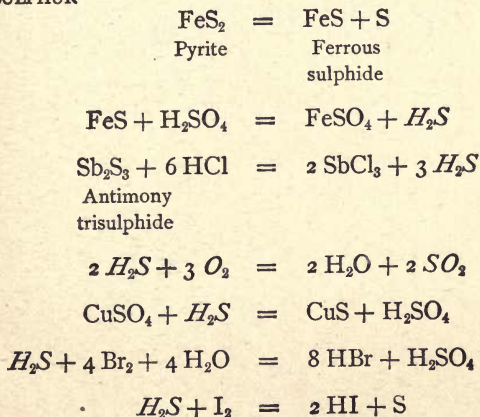
IODINE



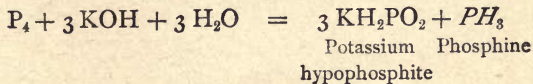
FLUORINE

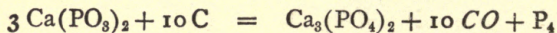
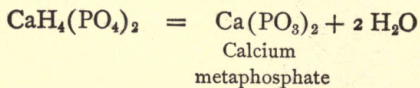
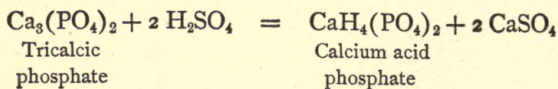
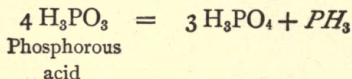
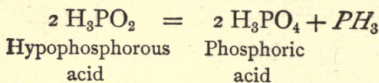
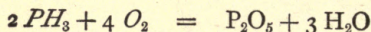


SULPHUR



PHOSPHORUS





APPENDIX F

VAPOUR PRESSURE OF WATER BETWEEN THE
TEMPERATURES 0° C. AND 100° C.

(TAKEN FROM DITTMAR'S CHEMICAL ARITHMETIC)

TEMP.	VAPOUR PRESSURE	TEMP.	VAPOUR PRESSURE.	TEMP.	VAPOUR PRESSURE.	TEMP.	VAPOUR PRESSURE.
0°	4.57						
1	4.91	26	24.96	51	96.66	76	301.09
2	5.27	27	26.47	52	101.55	77	313.85
3	5.66	28	28.07	53	106.65	78	327.05
4	6.07	29	29.74	54	111.97	79	340.73
5	6.51	30	31.51	55	117.52	80	354.87
6	6.97	31	33.37	56	123.29	81	369.51
7	7.47	32	35.32	57	129.31	82	384.64
8	7.99	33	37.37	58	135.58	83	400.29
9	8.55	34	39.52	59	142.10	84	416.47
10	9.14	35	41.78	60	148.88	85	433.19
11	9.77	36	44.16	61	155.95	86	450.47
12	10.43	37	46.65	62	163.29	87	468.32
13	11.14	38	49.26	63	170.82	88	486.76
14	11.88	39	52.00	64	178.86	89	505.81
15	12.67	40	54.87	65	187.10	90	525.47
16	13.51	41	57.87	66	195.67	91	545.77
17	14.40	42	61.02	67	204.56	92	566.71
18	15.33	43	64.31	68	213.79	93	588.33
19	16.32	44	67.76	69	223.37	94	610.64
20	17.36	45	71.36	70	233.31	95	633.66
21	18.47	46	75.13	71	243.62	96	657.40
22	19.63	47	79.07	72	254.30	97	681.88
23	20.86	48	83.19	73	265.38	98	707.13
24	22.15	49	87.49	74	276.87	99	733.16
25	23.52	50	91.98	75	288.76	100	760.00

APPENDIX G

TO FIND THE LOGARITHMS OF A NUMBER

RULE.—*Regard the number Q as separated into two factors $q \times 10^{\pm n}$, where q begins in the units' place. Find in the tables the logarithm of q. This will be the mantissa of the desired logarithm. Prefix to this the characteristic or index $\pm n$.*

A few examples will sufficiently elucidate the process.

Example.—Desired the logarithm to four decimal places of the number 306.

Write the number, or, better, merely consider it as if factored in the form $3.06 \cdot 10^2$. In the four-place table, on the line 3.0 and in the column headed 6 will be found .4857, which is $\log 3.06$. Obviously, $\log 10^2 = 2$. Therefore $\log 306. = \log 3.06 + \log 10^2 = .4857 + 2$, which is usually written 2.4857.

Further Examples. Interpolation.—Desired to four decimal places the logarithm of 306.2.

This will lie between the logs of 306 and 307 (and approximately 0.2 of the way), and as the table is not carried out further we must interpolate.

For 3.07 we find	.4871		Difference = .0014, usually written
For 3.06 we find	.4857	ten	14.
Interpolation, 0.2 of 14			The desired mantissa will be 0.2
= 2.8 =	3		of the way from .4857 to .4871.
$\therefore \log 3.062 =$.4860		Hence we must add to the former
$\therefore \log 306.2 = \log 3.062 + \log 10^2$			number 0.2 · 14. = 3.
= 2.4860			

The interpolation may always be made by subtracting and multiplying as in this example, but to save the labour, log-

arithm tables are usually provided with marginal interpolation tables, by the aid of which interpolations may easily be made mentally.

Thus in taking out $\log 3.062$ we find $\log 3.06 = .4857$. By inspection, difference = 14. In the interpolation table headed 14, line 2, stands 3, which is therefore the desired 0.2 of 14. Therefore $\log 3.062 = .4860$. This operation could, of course, be carried out mentally.

The present tables are arranged so that the interpolation tables stand opposite, or nearly so, to the logarithms to which they correspond. This not only gives them a convenient location, but enables the computer usually to avoid even the mental subtraction of the successive logarithms to find the difference, since this will, of course, be that at the head of the nearest difference table. Usually also the error introduced by using an interpolation table slightly too large or too small is negligible.

FOUR PLACE LOGARITHMS.

No.	0	1	2	3	4	5	6	7	8	9	INTERPOLATION TABLES.
1.00	.0000	.0004	.0009	.0013	.0017	.0022	.0026	.0030	.0035	.0039	38 36 34 32
.01	.0043	.0048	.0052	.0056	.0060	.0065	.0069	.0073	.0077	.0082	4 4 3 3
.02	.0086	.0090	.0095	.0099	.0103	.0107	.0111	.0116	.0120	.0124	8 7 7 6
.03	.0128	.0133	.0137	.0141	.0145	.0149	.0154	.0158	.0162	.0166	11 11 10 10
.04	.0170	.0175	.0179	.0183	.0187	.0191	.0195	.0199	.0204	.0208	15 14 14 13
.05	.0212	.0216	.0220	.0224	.0228	.0233	.0237	.0241	.0245	.0249	19 18 17 16
.06	.0253	.0257	.0261	.0265	.0269	.0273	.0278	.0282	.0286	.0290	23 22 20 19
.07	.0294	.0298	.0302	.0306	.0310	.0314	.0318	.0322	.0326	.0330	27 25 24 22
.08	.0334	.0338	.0342	.0346	.0350	.0354	.0358	.0362	.0366	.0370	30 29 27 26
.09	.0374	.0378	.0382	.0386	.0390	.0394	.0398	.0402	.0406	.0410	34 32 31 29
1.0	.0000	.0043	.0086	.0128	.0170	.0212	.0253	.0294	.0334	.0374	30 28 26 24
.1	.0414	.0453	.0492	.0531	.0569	.0607	.0645	.0682	.0719	.0755	3 3 3 2
.2	.0792	.0828	.0864	.0899	.0934	.0969	.1004	.1038	.1072	.1106	6 6 5 5
.3	.1139	.1173	.1206	.1239	.1271	.1303	.1335	.1367	.1399	.1430	9 8 8 7
.4	.1461	.1492	.1523	.1553	.1584	.1614	.1644	.1673	.1703	.1732	12 11 10 10
.5	.1761	.1790	.1818	.1847	.1875	.1903	.1931	.1959	.1987	.2014	15 14 13 12
.6	.2041	.2068	.2095	.2122	.2148	.2175	.2201	.2227	.2253	.2279	18 17 16 14
.7	.2304	.2330	.2355	.2380	.2405	.2430	.2455	.2480	.2504	.2529	21 20 18 17
.8	.2553	.2577	.2601	.2625	.2648	.2672	.2695	.2718	.2742	.2765	24 22 21 19
.9	.2788	.2810	.2833	.2856	.2878	.2900	.2923	.2945	.2967	.2989	27 25 23 22
2.0	.3010	.3032	.3054	.3075	.3096	.3118	.3139	.3160	.3181	.3201	22 20 18 16
.1	.3222	.3243	.3263	.3284	.3304	.3324	.3345	.3365	.3385	.3404	2 2 2 2
.2	.3424	.3444	.3464	.3483	.3502	.3522	.3541	.3560	.3579	.3598	4 4 4 3
.3	.3617	.3636	.3655	.3674	.3692	.3711	.3729	.3747	.3766	.3784	7 6 5 5

2.5	.3979	.3997	.4014	.4031	.4048	.4065	.4082	.4099	.4116	.4133	11	10	9	8
.6	4150	4166	4183	4200	4216	4232	4249	4265	4281	4298	13	12	11	10
.7	4314	4330	4346	4362	4378	4393	4409	4425	4440	4456	15	14	13	11
.8	4472	4487	4502	4518	4533	4548	4564	4579	4594	4609	18	16	14	13
.9	4624	4639	4654	4669	4683	4698	4713	4728	4742	4757	20	18	16	14
3.0	.4771	.4786	.4800	.4814	.4829	.4843	.4857	.4871	.4886	.4900	15	14	13	12
.1	4914	4928	4942	4955	4969	4983	4997	5011	5024	5038	2	1	1	1
.2	5051	5065	5079	5092	5105	5119	5132	5145	5159	5172	3	3	3	2
.3	5185	5198	5211	5224	5237	5250	5263	5276	5289	5302	5	4	4	4
.4	5315	5328	5340	5353	5366	5378	5391	5403	5416	5428	6	6	5	5
3.5	.5441	.5453	.5465	.5478	.5490	.5502	.5515	.5527	.5539	.5551	8	7	7	6
.6	5563	5575	5587	5599	5611	5623	5635	5647	5658	5670	9	8	8	7
.7	5682	5694	5705	5717	5729	5740	5752	5763	5775	5786	11	10	9	8
.8	5798	5809	5821	5832	5843	5855	5866	5877	5888	5899	12	11	10	10
.9	5911	5922	5933	5944	5955	5966	5977	5988	5999	6010	14	13	12	11
4.0	.6021	.6031	.6042	.6053	.6064	.6075	.6085	.6096	.6107	.6117	11	10	9	8
.1	6128	6138	6149	6160	6170	6180	6191	6201	6212	6222	1	1	1	1
.2	6232	6243	6253	6263	6274	6284	6294	6304	6314	6325	2	2	2	2
.3	6335	6345	6355	6365	6375	6385	6395	6405	6415	6425	3	3	3	2
.4	6435	6444	6454	6464	6474	6484	6493	6503	6513	6522	4	4	4	3
4.5	.6532	.6542	.6551	.6561	.6571	.6580	.6590	.6599	.6609	.6618	6	5	5	4
.6	6628	6637	6646	6656	6665	6675	6684	6693	6702	6712	7	6	5	5
.7	6721	6730	6739	6749	6758	6767	6776	6785	6794	6803	8	7	6	6
.8	6812	6821	6830	6839	6848	6857	6866	6875	6884	6893	9	8	7	6
.9	6902	6911	6920	6928	6937	6946	6955	6964	6972	6981	10	9	8	7

INTERPOLATION
TABLES.

No.	0	1	2	3	4	5	6	7	8	9	
5.0	.6990	.6998	.7007	.7016	.7024	.7033	.7042	.7050	.7059	.7067	9
.1	7076	7084	7093	7101	7110	7118	7126	7135	7143	7152	8
.2	7160	7168	7177	7185	7193	7202	7210	7218	7226	7235	7
.3	7243	7251	7259	7267	7275	7284	7292	7300	7308	7316	6
.4	7324	7332	7340	7348	7356	7364	7372	7380	7388	7396	5
5.5	.7404	.7412	.7419	.7427	.7435	.7443	.7451	.7459	.7466	.7474	4
.6	7482	7490	7497	7505	7513	7520	7528	7536	7543	7551	3
.7	7559	7566	7574	7582	7589	7597	7604	7612	7619	7627	2
.8	7634	7642	7649	7657	7664	7672	7679	7686	7694	7701	1
.9	7709	7716	7723	7731	7738	7745	7752	7760	7767	7774	0
6.0	.7782	.7789	.7796	.7803	.7810	.7818	.7825	.7832	.7839	.7846	9
.1	7853	7860	7868	7875	7882	7889	7896	7903	7910	7917	8
.2	7924	7931	7938	7945	7952	7959	7966	7973	7980	7987	7
.3	7993	8000	8007	8014	8021	8028	8035	8041	8048	8055	6
.4	8062	8069	8075	8082	8089	8096	8102	8109	8116	8122	5
6.5	.8129	.8136	.8142	.8149	.8156	.8162	.8169	.8176	.8182	.8189	4
.6	8195	8202	8209	8215	8222	8228	8235	8241	8248	8254	3
.7	8261	8267	8274	8280	8287	8293	8299	8306	8312	8319	2
.8	8325	8331	8338	8344	8351	8357	8363	8370	8376	8382	1
.9	8388	8395	8401	8407	8414	8420	8426	8432	8439	8445	0
7.0	.8451	.8457	.8463	.8470	.8476	.8482	.8488	.8494	.8500	.8506	9
.1	8513	8519	8525	8531	8537	8543	8549	8555	8561	8567	8
.2	8573	8579	8585	8591	8597	8603	8609	8615	8621	8627	7
.3	8633	8639	8645	8651	8657	8663	8669	8675	8681	8686	6
.4	8692	8698	8704	8710	8716	8722	8727	8733	8739	8745	5

7.5	.8751	.8756	.8762	.8768	.8774	.8779	.8785	.8791	.8797	.8802	3
.6	8808	8814	8820	8825	8831	8837	8842	8848	8854	8859	3
.7	8865	8871	8876	8882	8887	8893	8899	8904	8910	8915	4
.8	8921	8927	8932	8938	8943	8949	8954	8960	8965	8971	4
.9	8976	8982	8987	8993	8998	9004	9009	9015	9020	9025	5
8.0	.9031	.9036	.9042	.9047	.9053	.9058	.9063	.9069	.9074	.9079	6
.1	9085	9090	9096	9101	9106	9112	9117	9122	9128	9133	1
.2	9138	9143	9149	9154	9159	9165	9170	9175	9180	9186	1
.3	9191	9196	9201	9206	9212	9217	9222	9227	9232	9238	2
.4	9243	9248	9253	9258	9263	9269	9274	9279	9284	9289	2
8.5	.9294	.9299	.9304	.9309	.9315	.9320	.9325	.9330	.9335	.9340	3
.6	9345	9350	9355	9360	9365	9370	9375	9380	9385	9390	3
.7	9395	9400	9405	9410	9415	9420	9425	9430	9435	9440	4
.8	9445	9450	9455	9460	9465	9469	9474	9479	9484	9489	4
.9	9494	9499	9504	9509	9513	9518	9523	9528	9533	9538	5
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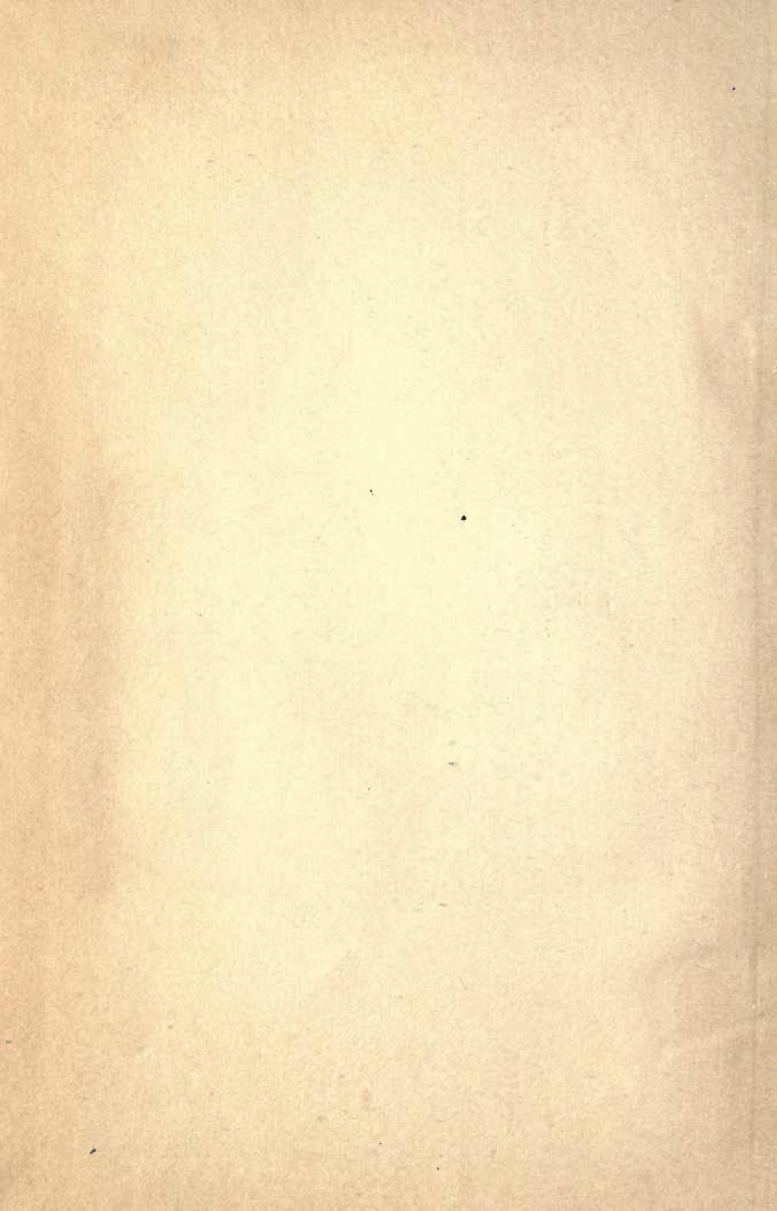
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